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An experimental and modeling study of acetylene-dimethyl ether mixtures oxidation at high-pressure

Lorena Marrodán, Ángela Millera, Rafael Bilbao, María U. Alzueta*

Aragón Institute of Engineering Research (I3A), Department of Chemical and Environmental Engineering, University of Zaragoza, R+D Building, Río Ebro Campus, 50018 Zaragoza, Spain



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ABSTRACT

The oxidation of acetylene (as soot precursor) and dimethyl ether (DME, as a promising fuel additive) mixtures has been analyzed in a tubular flow reactor, under high-pressure conditions (20, 40 and 60 bar), in the 450–1050 K temperature range. The effect of varying the air excess ratio ($\lambda \approx 0.7, 1$ and 20) and the percentage of DME with respect to acetylene (10 and 40%) has been analyzed from both experimental and modeling points of view. The addition of DME modifies the composition of the radical pool, increasing the production of OH radicals which cause a shift in the onset temperature for C_2H_2 conversion to lower temperatures; the higher the amount of DME, the lower the temperature. The presence of DME favors the oxidation of C_2H_2 towards products such as CO and CO_2 , eliminating carbon from the paths that lead to the formation of soot. On the other hand, in the presence of C_2H_2 , DME begins to be consumed at temperatures higher than those required for the high-pressure oxidation of neat DME, around 175–200 K more. Consequently, the negative temperature coefficient (NTC) region characteristic of this compound at low temperatures is not observed under those conditions. However, an additional analysis of the influence of DME inlet concentration (at 20 bar and $\lambda=1$) indicates that, if the amount of DME in the mixture is increased to 500 ppm and more (700 or 1000 ppm), the reaction pathways responsible for this high DME reactivity at low temperatures become more relevant and the NTC region can now be observed.

1. Introduction

Dimethyl ether (CH_3OCH_3 , DME) is the simplest ether, with a high oxygen content, high cetane number (55), low boiling point and no C–C bonds. It can be large-scale produced from non-renewable feedstocks such as natural gas or crude oil, but also from more environmentally friendly raw materials including waste products and biomass [1–3]. The promising properties make DME to be considered as a potential replacement fuel and/or diesel fuel additive [4]. Therefore, the use of DME has been experimentally studied in diesel engines, showing its advantages in terms of emissions and engine efficiency [5,6] and also from a computational point of view. Benajes et al. [7] showed the potential of using DME in compression ignition engines, maintaining the efficiency of diesel and achieving almost zero emissions of NO_x and soot.

Given the high expectations for DME use, its conversion has been widely analyzed in the last years, especially for its typical two-stage oxidation. In some studies, reactive species, such as ozone, are added to promote low-temperature reactivity and, thus, to achieve a better understanding of the low-temperature oxidation process [8]. The use of

DME, as a suitable combustion promoter for compression-ignition engines, has also been proposed in recent studies focused on the study of the combustion properties of ammonia (NH_3) as a promising carbon-free fuel for mobility and power generation [9,10]. Results from Rapid Compression Machines (RCM) indicated a significant shortening of the ignition delay times and an increase of NH_3 flame speeds [9], even when very low fractions of DME are mixed with NH_3 [10].

Several research works have been focused on the oxidation of DME and different hydrocarbons, evaluating the possibility of being used as an additive. Burke et al. [11] reported a promoting effect of DME on methane ignition at high-pressures (7–40 atm), mainly due to an increase in radical production at low temperatures from DME conversion. In the same line, Hashemi et al. [12] detected, in a high-pressure flow-reactor study, that the addition of DME to CH_4 (even small amounts as 530 ppm) causes an acceleration of its ignition, which is more noticeable for reducing conditions. This fact was also observed by Kaczmarek et al. [13], who found that DME forms radicals that contribute to decrease, under fuel-rich conditions, the onset temperature for the conversion of natural gas by 200 K. Song et al. [14], during ethane oxidation with the

* Corresponding author.

E-mail address: uxue@unizar.es (M.U. Alzueta).

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Table 1
Matrix of experimental conditions^a.

Set	C ₂ H ₂ [ppm]	DME [ppm]	O ₂ [ppm]	P (bar)	λ	t _r (s)
1	1056	107	2326	20	0.78	5–11.6
2	1018	382	3075	20	0.8	
3	1000	154	3063	20	1	
4	1033	317	4242	20	1.2	
5	1080	99	62,906	20	21	
6	1046	388	79,771	20	21.1	
7	1050	100	2034	40	0.7	9.9–23.2
8	1006	351	2975	40	0.83	
9	1023	105	2980	40	1	
9R	1131	114	3180	40	1	
10	1026	360	4885	40	1.34	
11	1040	119	52,730	40	17.8	
12	1082	340	79,437	40	21.3	
13	1088	98	2167	60	0.72	14.9–34.8
14	1091	380	2595	60	0.67	
15	1076	113	2943	60	0.97	
16	1031	323	4712	60	1.32	
17	1059	109	57,420	60	19.3	
18	1048	378	71,780	60	19.12	
19	1146	506	4248	20	0.97	5–11.6
20	1138	693	4780	20	0.97	
21	1147	1034	5661	20	0.95	

^a Experiments are conducted in the 450–1050 K temperature range. The balance is closed with N₂.

addition of DME, observed a decrease in aromatic species, key intermediates in soot formation, and the results obtained by Esarte et al. [15] showed a diminution in the formation of soot when DME was added to acetylene at atmospheric pressure. Moreover, the addition of 20% of DME to n-butane in a rapid compression machine (16–30 bar), at an equivalence ratio of 0.5, results in an increase of free radicals, so the reactivity of the system is enhanced, and air–fuel mixtures can be ignited at lower temperatures [16].

Despite the large number of studies on the effects of DME addition on the combustion properties of different hydrocarbons, there is a lack of works that analyze these effects on one of the simplest hydrocarbons, i.e. acetylene (C₂H₂). It is widely recognized as an intermediate in the conversion of higher hydrocarbons as well as a soot precursor [17,18]. In this line, a previous work of the present research group [19] analyzes the effect of DME addition to C₂H₂ oxidation, in a gas-phase installation at atmospheric pressure, from both experimental and modeling points of view. The results indicate that DME addition modifies the radical pool, acting as an inhibitor or promoter of C₂H₂ consumption depending mainly on the oxygen availability.

Furthermore, it is also important to broaden the range of experimental conditions towards those closer of modern diesel engines operation. Therefore, in this paper, the high-pressure oxidation of acetylene-DME mixtures is reported, which is of interest for diesel engines operating at high pressures. It will contribute to extend the knowledge of DME behavior as a possible fuel additive. This study has been performed in a quartz tubular flow reactor under high-pressure conditions, from both experimental and modeling points of view.

2. Experimental section

High-pressure oxidation experiments of C₂H₂-DME mixtures have been performed in an experimental setup previously used and widely described in preceding works of the group, addressing homogeneous high-pressure gas-phase reactions (e.g. [20,21]). Therefore, only a brief description of the main features is provided below.

The oxidation of C₂H₂ (approximately 1000 ppm) and DME (10 and 40% of addition with respect to C₂H₂, i.e. 100 or 400 ppm) mixtures has been carried out in a tubular flow reactor designed to approximate plug flow [22] (inner diameter of 6 mm and length of 1500 mm). Experiments were conducted in the temperature range of 450–1050 K, since this is the

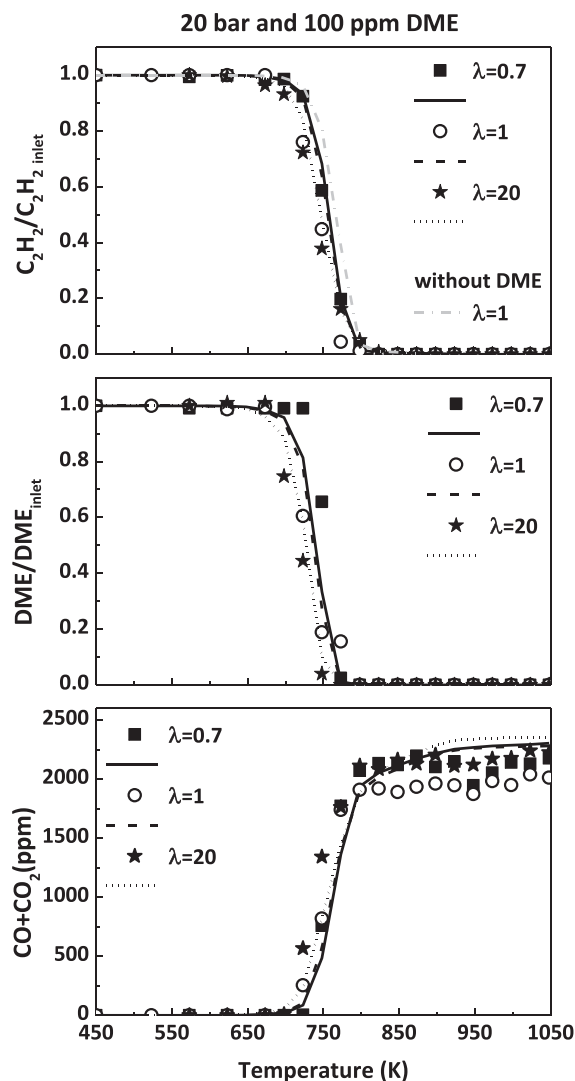


Fig. 1. Influence of the air excess ratio (λ) on the concentration profiles of C₂H₂, DME and CO+CO₂ as a function of temperature, for 20 bar and the lowest amount of DME tested (100 ppm). Conditions denoted as sets 1, 3 and 5 in Table 1.

range in which the conversion of both fuels, C₂H₂ and DME, takes place, as can be seen in the figures included in the results and discussion section. The influence of pressure and the oxygen availability has been evaluated. Three different manometric pressures have been tested (20, 40 and 60 bar) and the oxygen concentration at the reactor inlet has been varied from reducing to oxidizing conditions ($\lambda \approx 0.7, 1$ and 20, with λ being the inlet oxygen concentration divided by the stoichiometric, considering both components of the fuel mixture, C₂H₂ and DME). Additionally, for 20 bar and $\lambda=1$, the DME inlet concentration has been increased to 500, 700 and 1000 ppm, keeping the C₂H₂ concentration constant at 1000 ppm. Reactants, supplied from gas cylinders, are highly diluted in N₂ to minimize the possible thermal effects of the reaction. Table 1 lists the experimental conditions.

For the conditions denoted as set 9 in Table 1, the experiment was carried out in duplicated and designated as set 9R. Thus, for each temperature studied within the range considered, two results were obtained. The experimental error has been estimated by calculating the pooled standard deviation (the square root of the sum of squares of the error) associated with the C₂H₂ normalized concentration, as this is the selected way of displaying results for an easier comparison (e.g. Fig. 1) because not always the same reactant concentrations have been feed to

the system. It has been assumed that the experimental error does not depend on the temperature in the range considered. In this way, the pooled standard deviation obtained is 0.05, i.e. 5%.

The tubular reactor is enclosed in a stainless-steel tube which acts as a pressure shell. K-thermocouples have been positioned between the quartz reactor and this steel shell to measure the longitudinal temperature profiles (which can be found as [Supporting Information](#) in [20,21,23]), obtaining an isothermal (± 10 K) reaction zone of 56 cm. The gas flow rate was kept constant (1 L (STP)/min), resulting in a gas residence time (t_r) in the isothermal zone represented by equation (1).

$$t_r(s) = \frac{261 \cdot P(\text{bar})}{T(K)} \quad (1)$$

Downstream the reactor, the pressure of the system is reduced to atmospheric level before analysis, which has been performed using a micro gas chromatograph (Agilent 3000A) equipped with thermal conductivity detectors and an ATI Mattson Fourier transform infrared (FTIR) spectrometer. The uncertainty of measurements can be estimated as $\pm 5\%$ for the GC and $\pm 10\%$ for the FTIR.

3. Chemical kinetic model

The experimental results have been analyzed in terms of a chemical kinetic mechanism, that was already able to describe with success the oxidation of DME under high-pressure conditions [21]. Since no modifications have been made to this mechanism and because a complete picture of the mechanism can be found in Marrodán et al. [21], only a description of the most relevant features is provided below.

A gas-phase reaction mechanism which describes C_1 - C_2 and NO interactions, first proposed by Glarborg et al. [24] in 1998, and accordingly revised and modified (e.g. [25]), represents the basis of the mechanism used in the present work. Furthermore, in the process of construction of the mechanism used here, reaction subsets for different oxygenates and relevant intermediate species were progressively incorporated, revised and updated. In this way, several reaction subsets for small organic compounds such as ethanol, C_2H_2 , DME and so on, were previously tested and validated under atmospheric-pressure conditions [19] and references therein, and, subsequently, under high-pressure conditions [20,21,23,26].

Specifically, in the case of the two compounds of interest for this study, the C_2H_2 reaction subset was proposed by Alzueta et al. [27] in an atmospheric gas-phase oxidation study, and later modified by Giménez-López et al. [17] to account for the high-pressure conditions. For DME, the Alzueta et al.'s reaction subset [28], validated at atmospheric pressure, was revised and updated according to more recent kinetic mechanisms from literature [11,29], that mainly proposed pressure dependencies for low-temperature oxidation pathways and to account for the high-pressure conditions [21]. Numerical calculations obtained with the whole mechanism, including those changes in DME subset, were compared against several sets of experimental data from literature covering a wide range of conditions and devices, such as shock tubes, rapid compression machines, jet-stirred reactors and flow reactors (for more details see Figs. S8-S17 in [Supplementary Material](#) of [21]). The model succeeded in depicting the main experimental trends.

Thus, the final mechanism used in the present work involves 138 species and contains 795 reactions. Model calculations have been performed using the Chemkin-Pro software package with the plug-flow reactor module [30] and considering the temperature profiles experimentally determined. Thermodynamic data have been taken from the same sources as the original mechanisms and has not been modified from [21].

4. Results and discussion

To evaluate the influence of the oxygen availability, different air excess ratios (λ) have been used for two concentrations of DME, 100 or

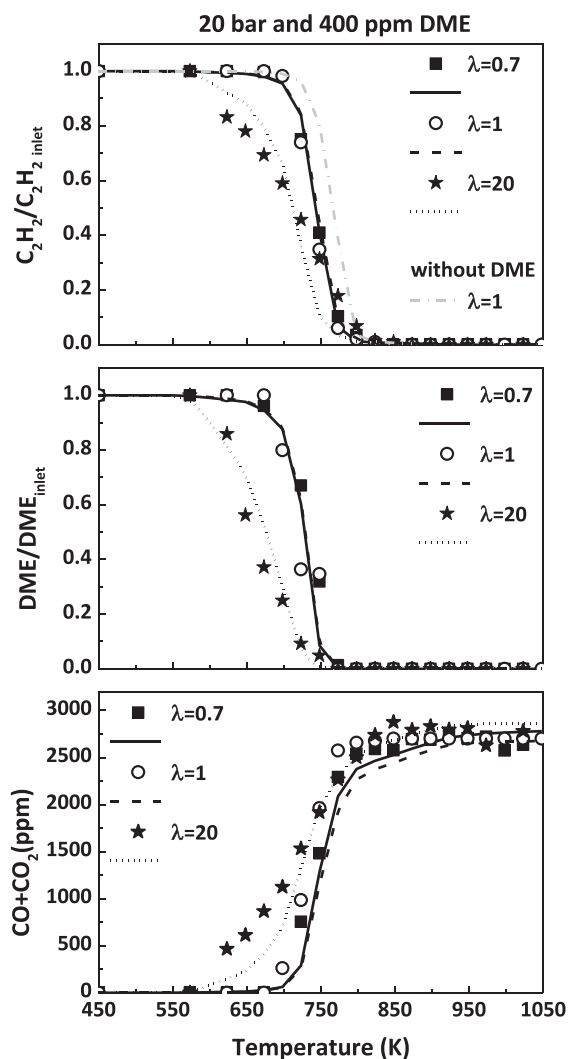


Fig. 2. Influence of the air excess ratio (λ) on the concentration profiles of C_2H_2 , DME and $CO+CO_2$ as a function of temperature, for 20 bar and the highest amount of DME tested (400 ppm). Conditions denoted as sets 2, 4 and 6 in [Table 1](#).

400 ppm, while keeping the pressure and the C_2H_2 concentration constant (1000 ppm). [Figs. 1 and 2](#) show the experimental results (symbols) and modeling calculations (lines) obtained at 20 bar, for the concentrations of C_2H_2 , DME, and the sum of CO and CO_2 , as the main products quantified. For the reactants C_2H_2 and DME, to facilitate comparison of results, concentrations have been normalized with respect to their inlet concentrations. For the other two pressures analyzed (40 and 60 bar), the trends are the same ([Figs. S.1 and S.2](#) in [Supplementary Material](#)) and, in general, the model reproduces the trends experimentally observed.

In [Fig. 1](#), for a constant pressure (20 bar) and 100 ppm of DME, the onset temperature for C_2H_2 conversion is almost the same independently of the oxygen fed to the system as reactant. Similarly, a change in the air excess ratio value from $\lambda=0.7$ to $\lambda=1$, does not modify the DME conversion profile. Only for oxidizing conditions ($\lambda=20$), DME conversion is slightly shifted to lower temperatures, around 25 K. However, if the amount of DME in the mixture is increased up to 400 ppm ([Fig. 2](#)), this shifting is emphasized in the case of DME, and also observed in the C_2H_2 concentration profile. Both compounds, C_2H_2 and DME, start to be consumed at lower temperatures, around 100 K less, that is from 725 K ($\lambda=0.7$ and $\lambda=1$) to 625 K ($\lambda=20$), and consequently, it is also reflected

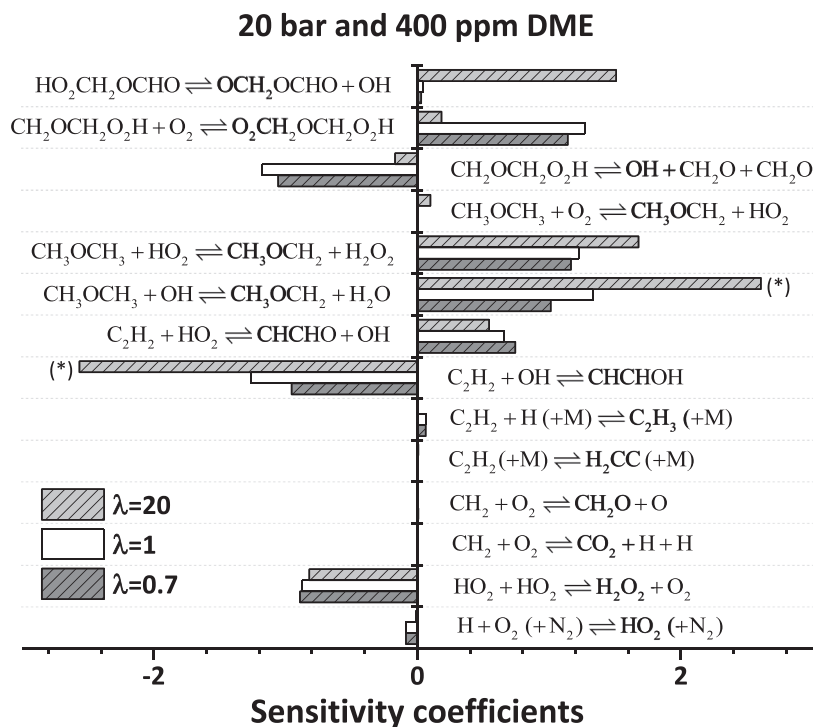


Fig. 3. First-order sensitivity analysis for CO for different air excess ratios, 400 ppm of DME and 20 bar. (*) sensitivity coefficients have been divided by two for a clearer representation. Sensitivity coefficients are given as $A_i \delta Y_j / Y_j \delta A_i$, where A_i is the pre-exponential constant for reaction i and Y_j is the mass fraction of j_{th} species.

in the concentration of CO and CO₂ (Fig. 2).

In the previous C₂H₂-DME mixtures oxidation study carried out at atmospheric pressure [19], in a flow reactor, and for the same percentages of DME added to the mixture (10 and 40% of C₂H₂), results indicate that the onset temperature for the conversion of C₂H₂ and DME depends on the oxygen availability, being lower for the highest value of λ considered and the highest amount of DME tested, similarly to the observations of the present work under oxidizing conditions.

In order to analyze the effect, if any, of DME addition on the conversion of C₂H₂, and since the mechanism provides a good description of the oxidation process of the mixtures, model calculations for C₂H₂ oxidation without DME have been performed. For a given pressure, there is no influence of the air excess ratio (Figs. S.3-S.5 in the [Supplementary Material](#)), what is in agreement with the findings of Giménez-López et al. [17] while studying the oxidation of C₂H₂ under similar conditions to those of this study. Thus, modeling results have been included in [Figs. 1 and 2](#) only for $\lambda=1$. It can be concluded that the presence of DME in the reactant mixture shifts the conversion of C₂H₂ to lower temperatures, and the higher the amount of DME, the lower the temperature at which reaction occurs.

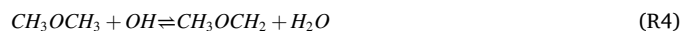
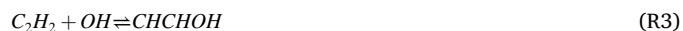
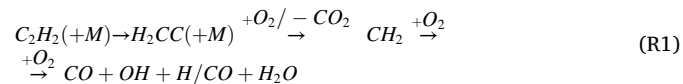
Compared to the temperature required for the oxidation of neat DME at high pressure [21], the onset temperature for DME conversion during the high-pressure oxidation of its mixtures with C₂H₂ is comparatively higher. Under the same conditions, for example, 20 bar and $\lambda=1$, neat DME starts to be consumed at around 525 K, while, when mixed with C₂H₂, its conversion does not start until 700–725 K (independently of DME concentration in the mixture).

In conclusion, C₂H₂ oxidation is shifted to lower temperatures in the presence of DME (promotion), whereas DME conversion is shifted to higher temperatures in the presence of C₂H₂ (inhibition).

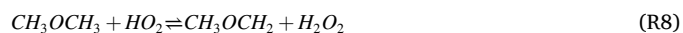
The main consumption routes for the reactants, C₂H₂ and DME, have been identified through several reaction rate analyses, that can help to explain the observations previously described. Under the present conditions, calculations indicate that the consumption routes for DME and C₂H₂ are almost the same than those previously described while analyzing the high-pressure oxidation of DME [21] and the oxidation of

other C₂H₂ mixtures, under high-pressure conditions too [17]. Therefore, only the main relevant routes are described below. The main reaction pathways are included in the [Supplementary Material](#) (Figs. S.6 and S.7).

Acetylene conversion is initiated by the sequence described in reaction R1, while the conversion of DME is started by reaction R2. Both initiation reactions represent a source of radicals, which later participate in the consumption of both C₂H₂ and DME. In the case of C₂H₂, to form the CHCHOH adduct (reaction R3), and in the case of DME, to obtain CH₃OCH₂ radical (reaction R4).

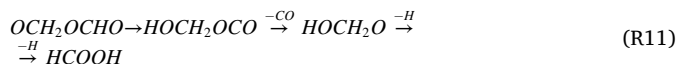
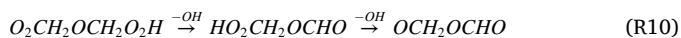
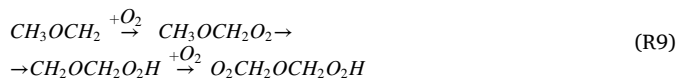


Hydroperoxyl radicals (HO₂), generated in reaction R2 and through the reaction of O₂ and HCO radicals (reaction R5), these latter produced from C₂H₂ and CHCHOH (reactions R6 and R7), also contribute to the generation of DME radicals (reaction R8).



Two different reaction pathways can be identified during DME conversion as stated in the previous DME high-pressure oxidation study [21]. One path that dominates at low temperatures and another at high temperatures. The first one is summarized in the R9–R11 reaction sequence and it is responsible of the high reactivity of DME at low

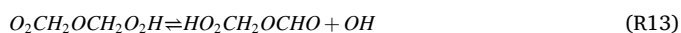
temperatures. In this mechanism, hydroperoxides formed by subsequent oxygen additions play an important role [31].



The second one, which dominates at high temperatures, starts with the β -scission of the $\text{CH}_2\text{OCH}_2\text{O}_2\text{H}$ radical forming two molecules of formaldehyde and hydroxyl radicals (reaction R12) and becomes more relevant as temperature increases. However, in the presence of C_2H_2 , the high-temperature DME oxidation pathways are dominant.



It has been previously stated that one of the effects of adding DME to the C_2H_2 oxidation is that its conversion starts at lower temperatures and, the higher the amount of DME, the lower the temperature. The main reason can be found in the OH radicals generated during the conversion of DME. Specifically, OH radicals are mainly produced in reaction R12 from the high-temperature mechanism, and reactions R13 and R14 from the low-temperature oxidation regime.



Depending on the oxygen availability and the amount of DME present in the mixture, DME addition modifies the radical pool composition, acting as an inhibitor or promoter, shifting the onset for C_2H_2 conversion to higher or lower temperatures, respectively, as was also observed at atmospheric pressure in [19]. That is, for $\lambda=0.7$, when DME is present in the mixture, less H radicals participate in C_2H_2 consumption through the H addition to form vinyl radicals ($\text{C}_2\text{H}_2 + \text{H} (+ \text{M}) \rightleftharpoons \text{C}_2\text{H}_3 (+ \text{M})$), and as a consequence, at atmospheric pressure, C_2H_2 conversion is shifted to higher temperatures; the higher the amount of DME in the mixture, the higher the temperature. However, for $\lambda=20$ the trend is the opposite, and both C_2H_2 and DME conversions are shifted to lower temperatures due to the increase in O and OH radicals. On the contrary, under the current high-pressure conditions, the formation of vinyl radicals is not as relevant as at atmospheric pressure, and the formation of OH and HO_2 radicals is favored.

The analysis of the main reaction pathways has been completed with a first-order sensitivity analysis for CO, 20 bar and the different air excess ratios analyzed. The highest concentration of DME has been selected since it is for which the most notable changes have been observed. Fig. 3 shows a comparison of the results obtained. Most of the sensitivity reactions identified correspond to DME and C_2H_2 consumption. In general, reactions involving DME and the species generated during its conversion have a promoting effect. It is noteworthy the effect of reaction R4, i.e. the initiation of DME oxidation, specially under oxidizing conditions.

Among the reactions with an inhibiting effect, there are two that involve the consumption of highly reactive radicals: reaction R3 and reaction R15. Reaction R3 implies the consumption of OH radicals generating CHCHOH, which later reacts with molecular oxygen (reaction R7) producing formic acid, a stable product. In the case of reaction R15, it also represents a sink of radicals, in this case of hydroperoxyl radicals (HO_2), which participate in the generation of DME radicals (reaction R8).



The sensitivity analysis has also been performed for the reactants,

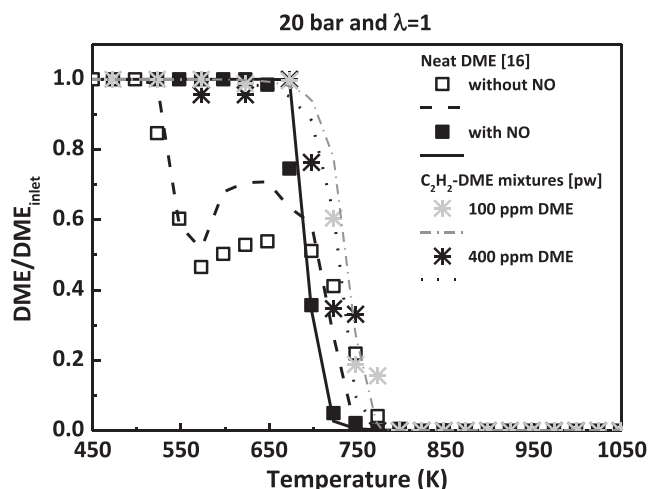


Fig. 4. Comparison of DME concentration evolution with temperature during the high-pressure oxidation of DME [21] and its mixtures with C_2H_2 [present work] in the same experimental setup.

DME and C_2H_2 , and the sensitivity reactions identified in both cases are almost the same as for CO, as it can be seen in Figs. S.8 and S.9 in the Supplementary Material.

DME is a suitable compound to be blended with low-reactivity fuels such as cyclopentane [32] because it is reactive at low temperatures, although this reactivity decreases with temperature (the well-known negative temperature coefficient (NTC) zone). However, unlike neat DME oxidation under high-pressure conditions [21], in the present work, during its oxidation in mixtures with C_2H_2 , also at high pressure, this NTC region is not clearly observed, neither from an experimental point of view nor kinetic modeling.

The issue of the appearance or not of the NTC region deserves a further discussion. To illustrate the different behaviors of DME oxidation, Fig. 4 shows a comparison of experimental and model results for DME consumption during its oxidation under high-pressure conditions with and without NO [21], and its mixtures with C_2H_2 . All the experiments shown have been carried out in the same experimental setup.

As it can be seen, during the high-pressure oxidation of DME in the absence of NO, in the 550–750 K temperature range, there is a zone where DME reactivity decreases with temperature.

This is due to a modification in the consumption routes for DME. As temperature increases, the β -scission of the $\text{CH}_2\text{OCH}_2\text{O}_2\text{H}$ radical (reaction R12) becomes more relevant preventing this radical to continue the reaction sequence above described as low-temperature reaction pathway (R9–R11).

However, the trends observed here related to the different DME concentrations during the high-pressure oxidation of its mixtures with C_2H_2 are more similar to the one previously described during its high-pressure oxidation in the presence of NO, where the NTC is not observed. This is due to the competition of DME radicals to continue reacting with O_2 and NO_2 . In the case of the C_2H_2 -DME mixtures, there is a competition of the reactants with the O_2 , and, as a consequence, DME conversion, in the presence of C_2H_2 , is shifted to higher temperatures where low-temperature reaction pathways are not so relevant.

Moreover, in previous studies in flow reactors (FR) at atmospheric pressure, this region did not appear neither during the oxidation of neat DME [28] nor in mixtures with C_2H_2 [19]. Nonetheless, an early reactivity of DME at very low temperatures was observed in a jet-stirred reactor (JSR) study [33]. Differences in the DME inlet concentration analyzed in both studies are significant: 20000 ppm in the case of the JSR and 500 ppm in both FR studies. Therefore, a more in-depth analysis of the influence of DME inlet concentration on the possible appearance of NTC behavior has been carried out. A complementary experimental

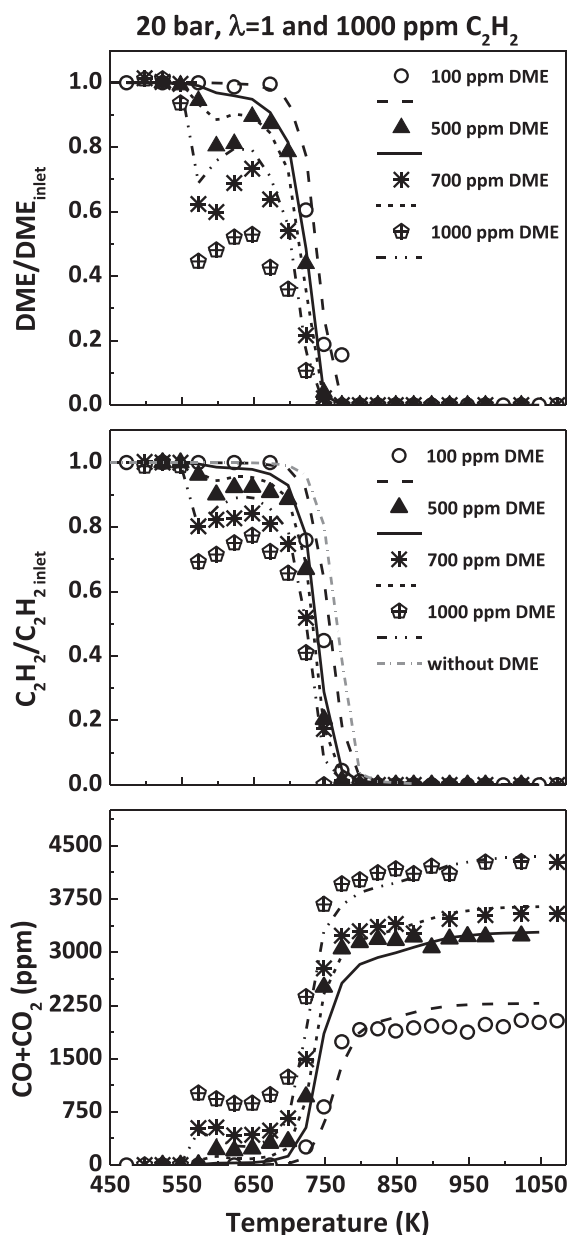


Fig. 5. Influence of inlet DME concentration on the concentration profiles of C_2H_2 , DME, and $CO+CO_2$ as a function of temperature during the high-pressure oxidation C_2H_2 -DME mixture oxidation, for the conditions denoted as sets 3, 19–21 in Table 1.

and modeling study has been performed for the conditions denoted as sets 19–21 in Table 1, i.e., 20 bar, stoichiometric conditions and 500, 700 and 1000 ppm of DME, while keeping constant the amount of C_2H_2 at 1000 ppm. Results are shown in Fig. 5.

In this case, even for the lowest amount of DME tested (500 ppm), the NTC zone is clearly observed, especially in the experimental concentration profile. This behavior is intensified by increasing the amount of DME in the mixture with C_2H_2 . It should be noted that, to compare the results, the variable λ must be kept constant, so if the amount of DME is increased, the amount of O_2 that is fed to the system must also be increased. Under these conditions (20 bar and $\lambda=1$), reaction rate analysis indicate that there is a DME amount threshold above which low-temperature reaction pathways (R9–R11 reaction sequence) are fast enough to play an important role in DME consumption. Otherwise, DME conversion only occurs in the high-temperature regimen through the

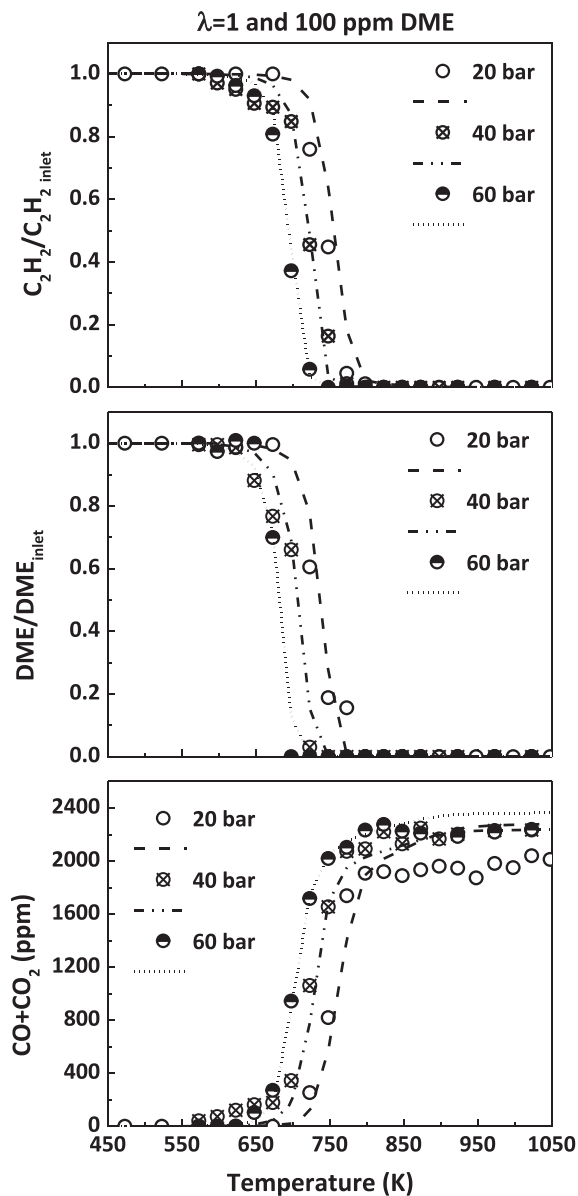


Fig. 6. Influence of pressure on the concentration profiles of C_2H_2 , DME, and $CO+CO_2$ as a function of temperature during the high-pressure oxidation of C_2H_2 -DME mixture oxidation, for the conditions denoted as sets 3, 9 and 15 in Table 1.

β -scission of $CH_2OCH_2O_2H$ radicals (reaction R12), as happens in the case of the mixtures with a content of 400 or 100 ppm of DME.

The influence of a change in the working pressure (20, 40 and 60 bar) during the oxidation of C_2H_2 -DME mixtures has also been evaluated in the present work. A comparison of experimental results and modeling calculations for stoichiometric conditions ($\lambda=1$) and 100 ppm of DME is shown in Fig. 6. For C_2H_2 , DME and the sum of CO and CO_2 , modeling calculations are in good agreement with the trends experimentally observed.

The onset temperature for C_2H_2 and DME conversion is shifted to lower temperatures as the working pressure is increased. This behavior was previously observed during the high-pressure oxidation of other mixtures with acetylene, for example, C_2H_2 -ethanol [23]. It is worth to mention that when pressure is increased from 20 to 40 bar or from 40 to 60 bar, for the same temperature, the gas residence time also increases (Equation (1)). As a consequence, the change in the onset temperature can be attributed both to the increase in pressure, and the consequent

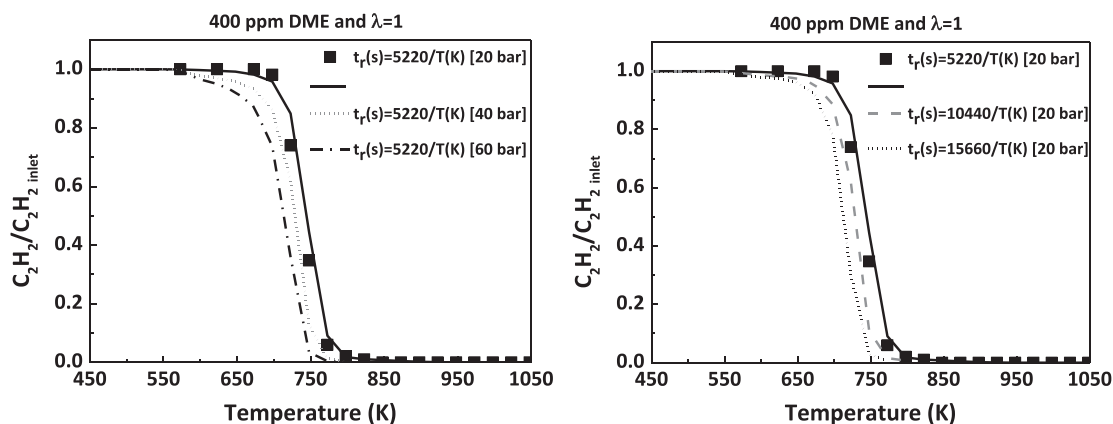


Fig. 7. Evaluation through model calculations of the effect of pressure (left) and gas residence time (right) on the C_2H_2 -DME mixtures conversion (400 ppm of DME), under stoichiometric conditions ($\lambda = 1$).

increase in the concentration of reactants, and to the related increase in the gas residence time. Previous works carried out under similar conditions in the same facility, have tried to elucidate which of the effects is predominant. For example, in an ethanol high-pressure oxidation work [26], results indicated that both pressure and gas-residence time had an appreciable effect displacing the conversion of ethanol to lower temperatures, if either of these two variables was increased. On the other hand, in a DME high-pressure oxidation work [21], the effect of the gas residence time was clearer and more noticeable than the effect of the pressure.

Modeling calculations, with the mechanism used in the present work, have been performed to try to distinguish between the effect of the pressure or the gas residence time, following the same approach of [21] and [26]. The results of this evaluation are shown in Fig. 7. The left side of the figure includes calculations made at different pressures (20, 40 and 60 bar) while keeping constant the gas residence time. On the other hand, the right side includes calculations made at constant pressure (20 bar) and different gas residence times. Results indicate that both the pressure and the gas residence time have an effect on acetylene conversion, which is shifted to lower temperatures if any of these variables is increased while keeping constant the other one. As a consequence, the aforementioned results of the influence of pressure on the conversion of C_2H_2 and DME correspond to the joint effect of both variables, pressure and residence time of the gas in the reaction zone.

In any case, what is highly relevant is that the modeling calculations in all the studies, including the present work and the previous ones, are able to represent the trends experimentally observed.

5. Conclusions

The high-pressure oxidation of C_2H_2 -DME mixtures has been analyzed in a tubular-flow reactor. The influence of several variables has been evaluated: pressure (20, 40 and 60 bar), oxygen inlet concentration (defined by different λ) and amount of DME in the reactant mixture. The experimental data have been compared with model calculations obtained with an in-house kinetic model developed, over the past years, by including different reaction subsets for small organic compounds in the basis mechanism. The final one obtained has been used successfully in previous studies, as well as in the present work.

For a constant pressure, regardless of the availability of oxygen, the onset temperature for C_2H_2 and DME conversion is almost the same, except for oxidizing conditions ($\lambda=20$), when both reactants start to be consumed at lower temperatures, up to 100 K less (for 400 ppm of DME).

The presence of DME in the reactant mixtures promotes the oxidation of C_2H_2 , whereas C_2H_2 inhibits the conversion of DME at low temperatures (for 100 and 400 ppm of DME).

The displacement of the C_2H_2 conversion to lower temperatures

(promotion) is due to an increase in the formation of OH radicals during the oxidation of DME; the higher the amount of DME, the lower the temperature at which C_2H_2 begins to be consumed. The addition of DME does not modify the oxidation regime of C_2H_2 , it only modifies the composition of the radical pool. As a consequence, the relevance of C_2H_2 reactions with OH increases, favoring the oxidation of C_2H_2 towards CO and CO_2 , and eliminating carbon from the reaction pathways that lead to the formation of soot.

A typical feature of DME oxidation is its high reactivity at low temperatures that decreases with temperature, the NTC region. However, it is not always present. When mixed with C_2H_2 , at 20 bar and $\lambda=1$, it seems that there is a DME concentration threshold above which the reactions that usually occur at these temperatures become relevant and this characteristic NTC region appears. For the lowest amounts of DME tested (100 and 400 ppm), high-temperature oxidation pathways predominate, and DME oxidation starts at temperatures comparatively higher than those required for its neat oxidation at high-pressures [21], approximately 175–200 K more. As a consequence of this shift to higher temperatures, the NTC region does not appear, indicating an inhibiting effect of C_2H_2 on the low-temperature oxidation of DME.

An increase in the working pressure shifts the onset temperature for C_2H_2 and DME conversion to lower temperatures. It is attributed to the increase in both the concentration of reactants and the gas residence time, due to an increase in pressure, rather than to a change in the pathways that control the reaction rate.

CRediT authorship contribution statement

Lorena Marrodán: Conceptualization, Methodology, Formal analysis, Investigation, Writing – review & editing. **Ángela Millera:** Writing – review & editing. **Rafael Bilbao:** Writing – review & editing. **María U. Alzuet:** Conceptualization, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

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

Data availability

Data are included as [supplementary material](#)

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2022.125143>.

References

- [1] 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; 87:1014–30.
- [2] Kohse-Höinghaus K, Oßwald P, Cool TA, Kasper T, Hansen N, Qi F, et al. Biofuel combustion chemistry: from ethanol to biodiesel. *Angew Chem Int Ed* 2010;49: 3572–97.
- [3] Azizi Z, Rezaeimanesh M, Tohidian T, Rahimpour MR. Dimethyl ether: a review of technologies and production challenges. *Chem Eng Process* 2014;82:150–72.
- [4] Semelsberger TA, Rodney LB, Greene HL. Dimethyl ether (DME) as an alternative fuel. *J Power Sources* 2006;156:497–511.
- [5] Ying W, Genbao L, Wei Z, Longbao Z. Study on the application of DME/diesel blends in a diesel engine. *Fuel Process Technol* 2008;89:1272–80.
- [6] Junjun Z, Xinqi Q, Zhen W, Bin G, Zhen H. Experimental investigation of low-temperature combustion (LTC) in an engine fueled with dimethyl ether (DME). *Energy Fuels* 2009;23:170–4.
- [7] Benajes J, Novella R, Pastor JM, Hernández-López A, Kokjohn S. Computational optimization of a combustion system for a stoichiometric DME fueled compression ignition engine. *Fuel* 2018;223:20–31.
- [8] Liao H, Kang S, Hansen N, Zhang F, Yang B. Influence of ozone addition on the low-temperature oxidation of dimethyl ether in a jet-stirred reactor. *Combust Flame* 2020;214:277–86.
- [9] Issayev G, Giri BR, Elbaz AM, Shrestha KP, Mauss F, Roberts WL, et al. Ignition delay time and laminar flame speed measurements of ammonia blended with dimethyl ether: a promising low carbon fuel blend. *Renewable Energy* 2022;181: 1353–70.
- [10] Dai L, Hashemi H, Glarborg P, Gersen S, Marshall P, Mokhov A, et al. Ignition delay times of NH₃/DME blends at high pressure and low DME fraction: RCM experiments and simulations. *Combust Flame* 2021;227:120–34.
- [11] Burke U, Somers KP, O’Toole P, Zinner CM, Marquet N, Bourque G, et al. An ignition delay and kinetic modeling study of methane, dimethyl ether, and their mixtures at high pressures. *Combust Flame* 2015;162:296–314.
- [12] Hashemi H, Christensen JM, Glarborg P. High-pressure pyrolysis and oxidation of DME and DME/CH₄. *Combust Flame* 2019;205:80–92.
- [13] Kaczmarek D, Herzler J, Porras S, Shaqiri S, Fikri M, Schuls C, et al. Plug-flow reactor and shock-tube study of the oxidation of very fuel-rich natural gas/DME/O₂ mixtures. *Combust Flame* 2021;225:86–103.
- [14] Song KH, Nag P, Litzinger TA, Haworth DC. Effects of oxygenated additives on aromatic species in fuel-rich, premixed ethane combustion: a modeling study. *Combust Flame* 2003;135:341–9.
- [15] Esarte C, Millera Á, Bilbao R, Alzueta MU. Effect of ethanol, dimethylether, and oxygen, when mixed with acetylene on the formation of soot and gas products. *Ind Eng Chem Res* 2010;49:6772–9.
- [16] Wu H, Shi Z, Lee C, Zhang H, Xu Y. Experimental and kinetic study on ignition of DME/n-butane mixtures under high pressures on a rapid compression machine. *Fuel* 2018;225:35–46.
- [17] Giménez-López J, Rasmussen CT, Hashemi H, Alzueta MU, Gao Y, Marshall P, et al. Experimental and kinetic modeling study of C₂H₂ oxidation at high pressure. *Int J Chem Kinet* 2016;48:724–38.
- [18] Frenklach M. Reaction mechanism of soot formation in flames. *Phys Chem Chem Phys* 2002;4:2028–37.
- [19] Marrodán L, Berdusán L, Aranda V, Millera Á, Bilbao R, Alzueta MU. Influence of dimethyl ether addition on the oxidation of acetylene in the absence and presence of NO. *Fuel* 2016;183:1–8.
- [20] Marrodán L, Millera Á, Bilbao R, Alzueta MU. High-pressure study of methyl formate oxidation and its interaction with NO. *Energy Fuels* 2014;28:6107–15.
- [21] Marrodán L, Arnal AJ, Millera Á, Bilbao R, Alzueta MU. The inhibiting effect of NO addition on dimethyl ether high-pressure oxidation. *Combust Flame* 2018;197: 1–10.
- [22] Rasmussen CL, Hansen J, Marshall P, Glarborg P. Experimental measurements and kinetic modeling of CO/H₂/O₂/NO_x conversion at high pressure. *Int J Chem Kinet* 2008;40:454–80.
- [23] Marrodán L, Fuster M, Millera Á, Bilbao R, Alzueta MU. Ethanol as a fuel additive: high-pressure oxidation of its mixtures with acetylene. *Energy Fuels* 2018;32: 10078–87.
- [24] Glarborg P, Alzueta MU, Dam-Johansen K, Miller JA. Kinetic modeling of hydrocarbon/nitric oxide interactions in a flow reactor. *Combust Flame* 1998;115: 1–27.
- [25] Glarborg P, Østberg M, Alzueta MU, Dam-Johansen K, Miller JA. The recombination of hydrogen atoms with nitric oxide at high temperatures. *Symp (Int) Combust* 1998;27:219–26.
- [26] Marrodán L, Arnal AJ, Millera Á, Bilbao R, Alzueta MU. High-pressure ethanol oxidation and its interaction with NO. *Fuel* 2018;223:394–400.
- [27] Alzueta MU, Borruey M, Callejas A, Millera A, Bilbao R. An experimental and modeling study of the oxidation of acetylene in a flow reactor. *Combust Flame* 2008;152:377–86.
- [28] Alzueta MU, Muro J, Bilbao R, Glarborg P. Oxidation of dimethyl ether and its interaction with nitrogen oxides. *Isr J Chem* 1999;39:73–86.
- [29] Zhao Z, Chaos M, Kazakov A, Dryer FL. Thermal decomposition reaction and a comprehensive kinetic model of dimethyl ether. *Int J Chem Kinet* 2008;40:1–18.
- [30] ANSYS Chemkin-Pro 17.2; Reaction Design: San Diego, 2016.
- [31] Wang Z, Herbinet O, Hansen N, Battin-Leclerc F. Exploring hydroperoxides in combustion: History, recent advances and perspectives. *Prog Energy Combust Sci* 2019;73:132–81.
- [32] Lokachari N, Wagnon SW, Kukkadapu G, Pitz WJ, Curran HJ. An experimental and kinetic modeling study of cyclopentane and dimethyl ether blends. *Combust Flame* 2021;225:255–71.
- [33] Rodriguez A, Frottier P, Herbinet O, Fournet R, Bounaceur R, Fittschen C, et al. Experimental and modelling investigation of the low-temperature oxidation of dimethyl ether. *J Phys Chem A* 2015;119:7905–23.