

# Study on the Repetitive Low-temperature Ignition Mechanism of DME/air Mixture in A Flow Reactor

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## 1 Introduction

As the simplest ether with higher cetane number of 55~60, DME exhibits typical two-stage oxidation behavior at low-temperature. To better understand this characteristic, a number of low-temperature oxidation kinetics studies have been conducted by using various reaction models, such as shock tubes [1], jet-stirred reactors [2,3], and flow reactors [4-8], in a wide range of temperature and equivalence ratio.

It should be noticed that most of these works adopted short reaction (residence) time (<4 seconds) and high dilution (around 97%) to the reactant mixtures. These methods well suppressed the possible self-induced ignitions or self-sustaining combustions in order to focus on the chemical stories. However, from practical standpoint, important combustion phenomenon might be neglected. For instance, most of these works considered that the oxidation reactions of DME started from 550 K at atmospheric pressure [7-8]. However, according to our previous work [9-10], auto-ignition under atmospheric pressure could be experienced below 550K with longer residence time (tens of seconds). It was also noticed that, the observed auto-ignition exhibited strong dependence on temperature and equivalence ratio. Gas analysis directly against the unsteady ignition process is needed to investigate the ignition mechanism and figure out the potential triggers that initial the ignition.

Therefore, recently, a new plug flow reactor, which enabled us to visually capture the ignition and flame propagation, was developed [11]. Description of the detailed combustion process with repetitive auto-ignition, flame propagation, and extinction at low-temperature can be found elsewhere [11]. In this paper, we present the gas analysis results conducted at multi positions along the reactor and at multi moments. Some important findings are reported in the body.

## 2 Experimental

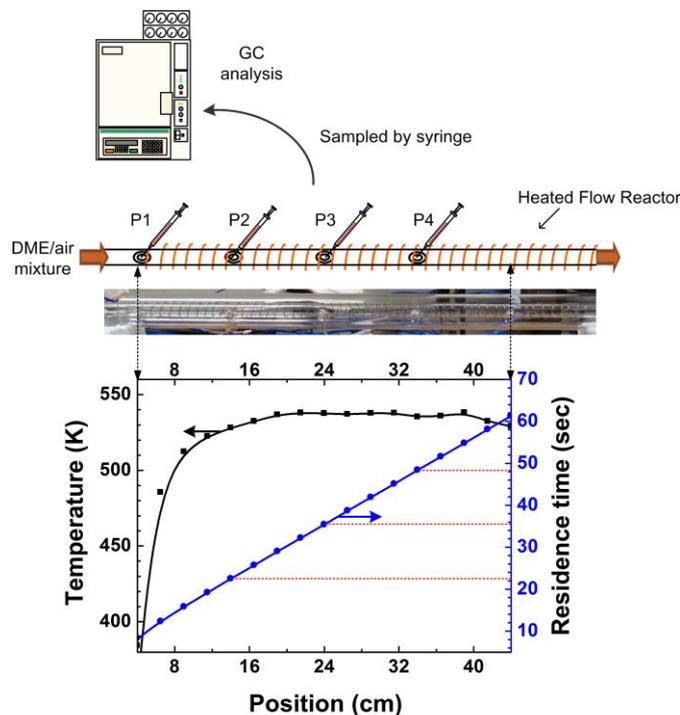


Figure 1. Schematic of experimental set-up, the centerline gas temperature profile for non-reactive condition at air flow rate = 29 ml/min, and the corresponding residence times along the reactor.

Figure 1 shows the schematic of the experimental set-up and the corresponding gas temperature along the centerline of the reactor. A 58 cm straight Pyrex tube (with inner diameter 12 mm and outer diameter 15 mm) was utilized as the plug flow reactor, in which premixed DME/air mixture was continuous flowing. Flow rate of DME was controlled by a mass flow rate controller (Kofloc model-5100), while flow rate of air was controlled by an orifice flow rate controlling system, which had been calibrated by a bubble flow meter (the accuracy is over 99%). Wire heater was uniformly surrounded the reactor from 4 cm to 54 cm to control the temperature. Thanks to the transparency of the Pyrex tube, flame could be visually observed. A digital video camera (Sony HDR-XR500, 30 frames per second) was used to record the ignition events. Prior to the experiments, the temperature profile on the centerline of the reactor was measured by K-type thermocouples (junction diameter of 1.5 mm) inserted from inlet and outlet at non-reactive condition with air (air flow rate = 29 ml/min, DME flow rate = 0 ml/min), as shown in figure 1.

Positions at 4 cm, 14 cm, 24 cm, and 34 cm from inlet are defined as P1, P2, P3 and P4, respectively. Through this study, the flow rate of the mixture gas was controlled as 29 ml/min. The corresponding residence times at different positions along the channel are also shown in figure 1. It takes 8 seconds, 23 seconds, 35 seconds and 48 seconds for the mixture gas to reach the positions P1, P2, P3 and P4, respectively. Gas was sampled at P1, P2, P3 and P4 by a 2.0-ml-volume Pyrex syringe (TOP type-0310) and then analyzed by a gas chromatograph (Shimadzu GC-14B) with a thermal conductivity detector (TCD). Note that the GC analysis was employed to determine the concentrations of stable species, but unable to identify any radical. The Syringe was preheated to 383 K to prevent possible condensations of the sample prior to injection. Hydrogen ( $H_2$ ), oxygen ( $O_2$ ), nitrogen ( $N_2$ ), methane ( $CH_4$ ) and carbon monoxide (CO) were separated by a molecule sieve 5A 80/100 column, and carbon dioxide ( $CO_2$ ), acetylene ( $C_2H_2$ ), formaldehyde (HCHO), dimethyl ether (DME), water ( $H_2O$ ), methyl formate ( $CH_3OCHO$ ), and formic acid ( $HCOOH$ ) were separated by a

Proapak T 50/80 column. Calibrations for HCHO, H<sub>2</sub>O, CH<sub>3</sub>OCHO, and HCOOH were conducted by using the vaporization gases of corresponding solutions.

Considering that the Reynolds number is extremely small ( $Re = 2.3$ ), there is no turbulence and the flow is governed by fully developed laminar state after a short distance (estimated as less than 2 mm) from inlet. Although radial velocity gradient exists, no difference in the gas analysis results was found at different radial positions as long as the sampling was conducted at the same axial position.

### 3 Results and discussion

#### 3.1 Repetitive ignition and flame propagation behavior

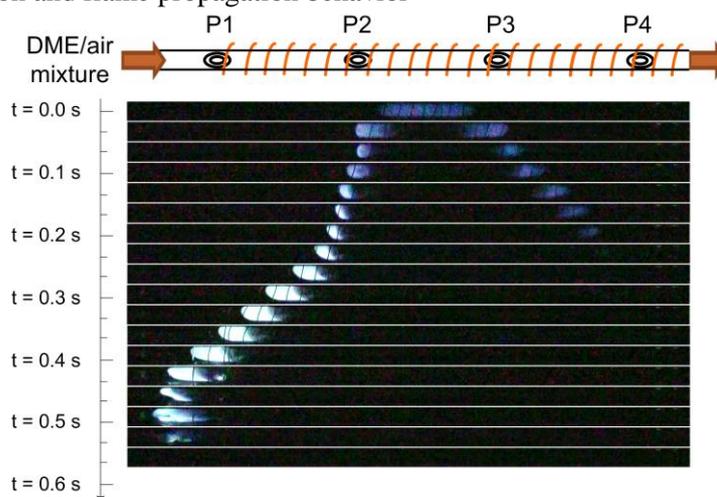


Figure 2. Flame images taken by video camera (equivalence ratio = 1.93).

As indicated in our previous work [11], the auto-ignition tends to occur at fuel rich conditions with equivalence ratio larger than 1.6. Figure 2 shows the flame images at the ignition moment at equivalence ratio of 1.93. Simply speaking, the ignition occurs at between P2 and P3, and then the ignition front propagates upstream and downstream. The flame is then quenched at the inlet. As the fresh mixture continuously flows in, the product gas (resulted from the previous ignition) is pushed to the downstream and simultaneously mixed with the incoming fresh mixture. Then, following some time delay, re-ignition occurs at the ignition position. This cycle is regularly repeated with some certain periodic duration.

As shown in figure 2, the ignition and subsequent flame propagation is completed within 0.6 second, while the periodic duration to induce each ignition is 50 seconds. To investigate the ignition mechanism, gas was sampled and analyzed by a GC at multi positions along the reactor (at P1, P2, P3, and P4) and time sequentially (at the moments of 27 seconds before the ignition, 5 seconds before the ignition, and 2 seconds after the ignition). The results are discussed in the following paragraph.

#### 3.2 Gas analysis results

For gas sampling, rapid extraction was accomplished within one second ( $< 1.0$  s) to ensure that the sampling was made at the objective sampling moment. Considering the sampling volume (1.0 ml) is much smaller than the volume of the reactor tube (about 66 ml), the disturbance to the flow field is considered as negligible.

Given that the periodic duration of the selected repetitive ignition behavior was 50 seconds, two sampling moments were set at 27 seconds and 5 seconds before the ignition occurrence, respectively.

It takes about 23 seconds for the mixture to reach P2, therefore, at the moment of 27 seconds before the ignition (i.e., 23 seconds after the last ignition), the fresh mixture just reaches P2 and but not reach P3 yet; while at 5 seconds before the ignition (i.e., 45 seconds after the last ignition), fresh mixture has already flowed past P3 that the mixing between fresh mixture and product gas has already got sufficient in the ignition zone, and the gas atmosphere there should be close to the state giving rise to the following ignition. The reason to pick these two sampling moments is that, the comparison between the gas compositions at these two moments is expected to reveal the ignition initiation mechanism as well as the effect of back diffusion in such low flow rate system.

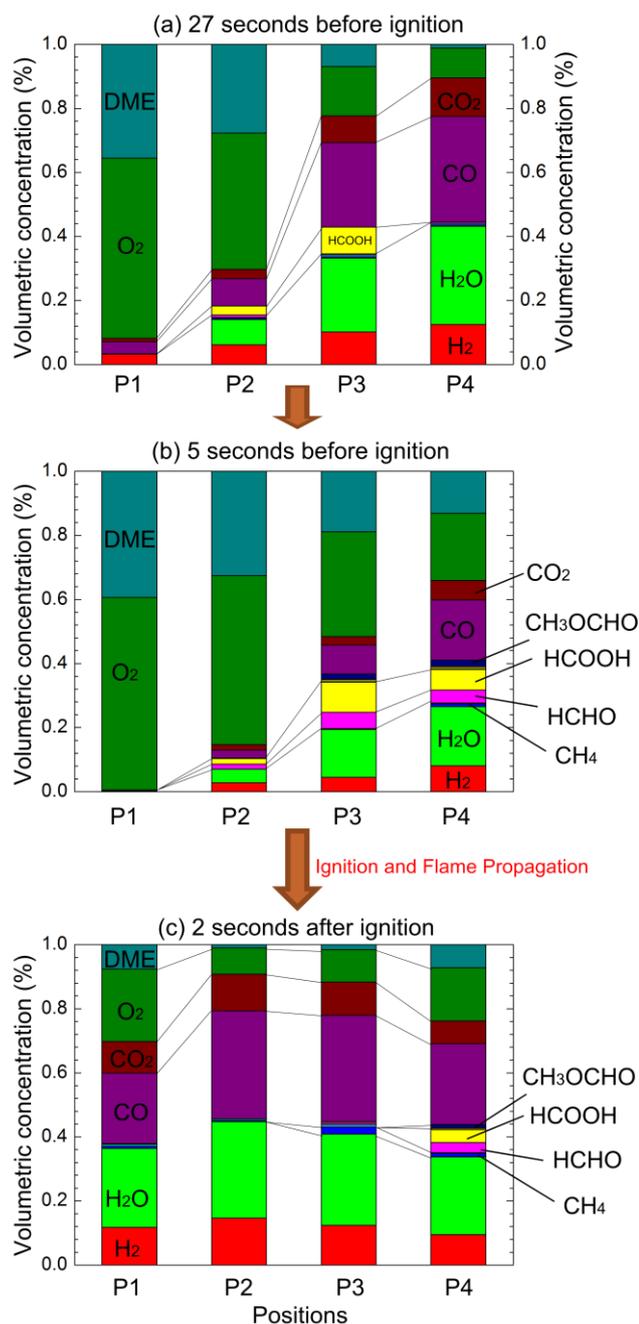
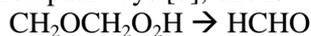


Figure 3. GC analysis results.

Figure 3 shows the gas analysis results. The volumetric concentrations have been normalized excluding  $N_2$ . In figure 3(a), at the moment of 27 seconds before ignition, the fresh mixture has already reached P2, however, due to the mixing between the fresh mixture and the product gas, certain amount of product gas of the previous ignition, such as  $H_2$ ,  $CO$  and  $CO_2$ , still exist at P1. Gas compositions at P3 and P4 are still dominated by these ignition product species. One interesting finding is that, certain amount of  $HCOOH$  was found at P2 and P3, however, other intermediates from mild oxidation did not appear, such as  $HCHO$ .  $HCOOH$  and  $HCHO$  have been considered as two label species during DME oxidation at low-temperature. The chain branching precursor,  $CH_2OCH_2O_2H$  follows two decomposition pathways [7], one is



and the other one is:



Since  $HCOOH$  at P3 should be pushed from upstream, therefore,  $HCOOH$  should be originally formed at around P2. Considering that the temperature at P2 (534 K) is 9 K lower than that at P3 (543 K) and no apparent  $HCHO$  formed at this moment, it is implied that there should be a critical temperature exist between 534 K and 543 K determines the reaction pathways of  $CH_2OCH_2O_2H$  decomposition: under this critical temperature,  $CH_2OCH_2O_2H$  follows the way forming  $HCOOH$ ; while above that, formation of  $HCHO$  dominates.

In figure 3(b), as the fresh mixture flows from P2 to downstream, the formation of  $HCOOH$  at P3 does not change too much, however, the formation of  $HCHO$  obviously increases. It should be noticed that fuel (DME) and oxygen have already exist at the ignition position, but the ignition does not occur until 50 seconds delay. This indicated that the initialization mechanism is not simply the oxidation of DME, rather, the back diffusion affects. It shows that the concentration of  $HCHO$  reaches its peak value at around P3. Since  $HCHO$  acts as one of major products resulted from chain-propagation way, the accumulation of  $HCHO$  there is possible to inhibit the chain-propagation way, thus enhanced the chain-branching way inducing the ignition.

Figure 3(c) shows the concentrations after ignition.  $CO$ ,  $CO_2$ ,  $H_2$ ,  $H_2O$ , and  $CH_4$  have been confirmed to act as major species from ignition [10]. Concentrations of these species follow decreasing trend from P2 to P4 except for  $CH_4$ , the concentration peak of which appears at P3. Generally speaking,  $CH_4$  is considered to be formed from the oxidation of  $HCHO$  in DME oxidation [12]. The concentration peak of  $CH_4$  should be caused by the higher accumulation of  $HCHO$  at P3 before ignition. The ignition initiation can be marked as formation of  $CH_4$ , however, the essential mechanism may not be the oxidation of  $HCHO$  or  $HCOOH$ , because it really exist  $HCHO$  and  $HCOOH$  at downstream (P4), but the flame propagation never reaches there.

## 4 Conclusions

The auto-ignition of DME/air mixture was investigated in a flow reactor at atmospheric pressure. Based on the visually captured ignition and flame propagation, gas compositions before and after the ignition were detected by GC at multi positions along the reactor.  $HCOOH$  and  $HCHO$  present different concentration profiles, which indicated that there should be a critical temperature exists between 534 K and 543 K determines the reaction pathways of the chain-branching precursor's decomposition. Due to the influence of back diffusion in this low flow rate system, the local accumulation of  $HCHO$  is probably one of the reason induced the auto-ignition at such low temperature. Only stable species have been detected by the present system, numerical validation focused on the radical species is expected in the future to reveal the auto-ignition mechanism.

## 5 Acknowledgments

This work is supported by JSPS-CAS Bilateral Joint Project (2012.4-2014.3) and Iwatani Naoji Foundation's Research Grant (2012.1-2014.3). Authors would like to express our sincere thanks to their supports.

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