Study on Reactivities of Refregirants R32, R125 and R410A using a Micro Flow Reactor with a Controlled Temperature Profile

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1 Introduction

In recent years, the use of chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) refrigerants are regulated to suppress the destruction of the ozone layer. CFC and HCFC refrigerants are being replaced to hydrofluorocarbon (HFC) refrigerants. At present, a HFC refrigerant R410A, which is a mixture of R32 (CH_2F_2, difluoromethane) and R125 (C_2HF_5, pentafluoroethane), is a mainstream due to its zero ozone depletion coefficient. This mixed refrigerant is used as an alternative refrigerant of CFC and HCFC in many applications because the global warming potential is relatively small. However, it is required to clarify the ignition and combustion characteristics of R32 for safety purpose since it is known as flammable [1]. Takizawa et.al studied laminar flame speeds of R32 based on the measurement of spherical propagation flame [2]. A chemical reaction model of HFCs including refrigerants of R32 and R125 has been constructed by NIST group [3]. On the other hand, ignition characteristics of HFCs are rarely studied. One of the reasons is that it is difficult to test ignition characteristics of HFCs with conventional experimental devices due to HFCs low reactivity and more essentially, the risk of exhaust gas that contains hydrogen fluoride (HF).

In this study, we employed a micro flow reactor with a controlled temperature profile (MFR) [4]. In MFR, a quartz tube with an inner diameter equal to or less than the quenching diameter of a test mixture is used as a reactor. The quartz tube is heated by an external heat source to give a steady temperature profile to the inner wall of the tube. A mixture of fuel and oxidizer flows into the heated reactor, and the flame is stabilized in the reactor. Since the flow inside the reactor is laminar and the pressure can be regarded as constant, it is possible to observe flame under well-defined condition. According to the previous study using this reactor [4, 5], three kinds of flames were observed depending on the flow velocity; that is, a normal flame in a high flow velocity region, a flame with repetitive extinction and ignition (FREI) in an intermediate flow velocity region, and a steady weak flame in the extremely low flow velocity region. Gas-phase temperature in a reactor depends strongly on the reactor wall temperature particularly in low flow velocity because the tube inner diameter is sufficiently small. Theoretical study [6] shows that weak flame is advantageous for evaluating the ignition characteristics of test fuels. In addition, it is possible to stabilize flames of weakly flammable mixture since reactor temperature is maintained by an external heat source.

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From these special characteristics, weak flame of ammonia [7] was examined in addition to conventional fuels (e.g., methane [5], n-heptane [8], etc.). To date, we have examined the ignition characteristics of fluoride refrigerants based on weak flames of pure R32 (CH_2F_2) [9] and R125 (C_2HF_5) [10]. Thus this study tries to address the ignition characteristics of R410A which is a mixed refrigerant of R32 and R125.

In this study, our goal is to clarify the effect of the mixing ratio of R32 and R125 on the overall ignition characteristics. Observation and analysis of weak flame structure of CH_2F_2/C_2HF_5/air mixture will be conducted using MFR. For comparison purpose, pure CH_2F_2 and C_2HF_5 will also be addressed.

2 Experimental setup and computational method

A schematic of the experimental setup is shown in Fig. 1. A quartz tube with an inner diameter of 2 mm and an outer diameter of 4 mm was used as a reactor. Note that quenching distance of R32 was 7.55 cm at equivalence ratio of 1.27 [11], and those of R410A and R125 were scarce to the author's knowledge. A steady temperature profile was given to the reactor using a H_2/air premixed flat flame burner and a maximum temperature of the inner surface of tube was 1300 K. Stoichiometric CH_2F_2/C_2HF_5/air mixtures of three kinds of mixing ratios were introduced into the reactor at a flow velocity of 2.0 cm/s, and flame observations were conducted. The three mixing ratios were 100 wt% of CH_2F_2, 50 wt% of CH_2F_2 and 50 wt% of C_2HF_5 (R410A), and 100 wt% of C_2HF_5. For each gas mixture, the mass ratios of CH_2F_2 and C_2HF_5 are simply described hereafter as 100:0, 50:50 and 0:100. For obtaining equivalence ratio, overall reaction (1) was used:

$$\mathrm{a}\, CH_2F_2 + \mathrm{b}\, C_2HF_5 + (\mathrm{a}+\mathrm{b}) O_2 => (\mathrm{a}+0.5\mathrm{b})\, CO_2 + (2\mathrm{a}+\mathrm{b})\, HF + \mathrm{b}\, CF_2O + 0.5\mathrm{b}\, CF_4 \qquad (1)$$

The a and b indicate the molar ratio of CH_2F_2 and C_2HF_5, respectively. An overall reaction of 100:0 was shown at a = 1.0, b = 0.0, and an overall reaction of 0:100 was shown at a = 0.0, b = 1.0. To capture images of weak flames in the reactor, a CH band-pass filter (Central wavelength 431.5 nm, full width at half maximum of 6.5 nm) was attached to a digital still camera (Nikon, D810). The weak flame position in the experiment was defined as the maximum brightness of chemiluminescence profile obtained from the flame image.

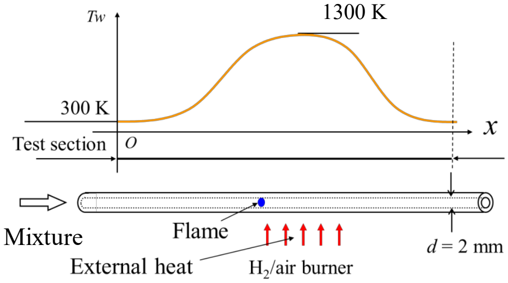

Fig.1 Schematic of experimental setup.

To simulate a reactor system, one-dimensional steady-state reactive flow calculation was conducted using modified flame code PREMIX in ANSYS Chemkin-Pro v17.2. A heat transfer term between gas phase and wall was added to the energy equation of PREMIX. The experimental temperature profile of the tube wall was given to the computaion. A detailed reaction mechanism developed by Linteris et al. [3] hereafter termed as Linteris mechanism was used for the all computation. The mechanism is composed of elementary reactions of C1 and C2 fluorohydrocarbons [158 species, 1384 reactions] based on USC Mech version II [109 species, 784 reactions] [12]. Linteris mechanism has shown a good agreement in the previous study on weak flames of pure CH_2F_2 [9] and C_2HF_5 [10]. The computational conditions were the same as the experimental conditions and the computational flame position was defined as the peak position of the heat release rate (HRR). In order to discuss further details, computations were also conducted in the case of the mass ratios of CH_2F_2 and C_2HF_5 (CH_2F_2:C_2HF_5) of 75:25 and 25:75 in addition to the conditions of the experiments.

3 Results and discussion

3.1 Weak flame positions and comparison between experimental and computational results

Figure 2 shows experimental weak flame image, brightness profile (solid line) and computational HRR profile (dotted line) calculated by the Linteris mechanism under the conditions of 100:0 (CH_2F_2 100%), 50:50 (CH_2F_2 50%, C_2HF_5 50%) and 0:100 (C_2HF_5 100%). The brightness profiles obtained by the experiments were normalized with the maximum values. First, weak flame of 100:0 shows a two-stage oxidation in which small luminescence is observed at around 1265 K (x = 4.3 cm) in the upstream of bright luminescence at around 1280 K (x = 4.6 cm). This was reproduced by computation using the Linteris mechanism. In the case of 0:100, the first luminescence is observed around 1200 K (x = 3.96 cm) and another very bright zone over a wide range is observed at the higher temperature side (x > 4.6 cm). For this bright zone of the case of 0:100, spectroscopic analysis was conducted and clarified that the zone is supposed to be induced by surface reaction of Si and remained F radical [13] there. Therefore, the first luminescence for this case is defined as the position of weak flame. In the case of 50:50, there was no significant change in chemiluminescence profile with that of 100:0. In this case, very bright zone was not seen in the downstream region. Weak flame positions of 50:50 slightly shifted to the downstream side compared with 100:0. Because weak flame positions of 0:100 shifted significantly to the lower temperature side, it was suggested that the weak flame position significantly changes with the amount of C_2HF_5 in the mixed refrigerants. Such a trend was further discussed by computations with Linteris mechanism shown in Fig. 2.

To address the effect of the mixing ratio of refrigerant on weak flame position with higher resolution, computational HRR profiles of 75:25 and 25:75 were shown in addition to those of 100:0, 50:50 and 0:100. In Fig.2, two HRR peaks were obtained in the cases of 100:0, 75:25 and 50:50, and one HRR peak was obtained only on low temperature side in the cases of 25:75 and 0:100. When the ratio of C_2HF_5 is increased from 100:0, the second HRR peak on the high temperature side shifted to the high temperature side up to 50:50 and then the second HRR peak value decreases gradually. During the change, the first HRR peak does not change largely. On the other hand, when C_2HF_5 addition is more than 50 wt%, the second HRR peaks become very small and only the first peaks at lower temperature side are observed. In the case of pure C_2HF_5 (0:100), a single HRR peak locates lower temperature side than the case of 25:75. From the above, it can be seen that the trend of the HRR peaks greatly changes at the condition of 50:50. These tendencies of computational weak flame positions are in good agreements with the experimental results for 100:0, 50:50 and 0:100.

3.2 Weak flame structures of 100:0, 50:50 and 0:100

Figure 3 shows the structures of weak flames in the cases of (a) 100:0, (b) 50:50 and (c) 0:100 to address the effect of mixture composition change on the flame structures. In the case of 100:0, refrigerant is consumed at the first HRR peak (x = 3.0 – 4.3 cm), CO, H_2O and CF_2O are produced as intermediates. CO is consumed at the second HRR peak (around x = 4.5 cm) and CO_2 is produced. For this condition, intermediates CF_2O and H_2O remain in the same fraction due to incomplete combustion. It was clarified that the reaction of $CF_2O + H_2O \Rightarrow CO_2 + 2HF$ proceeds if higher maximum wall temperature of 2000 K is employed [9]. On the other hand, in the case of 0:100, refrigerant is consumed and intermediates such as CO, H_2O, CHF_3 and C_2F_6 are produced at the first HRR peak (x = 3.0 – 4.3 cm). And then, H_2O and CHF_3 are consumed at the first HRR peak and there are few species containing H atoms except HF. That is, most of the H atoms contained in C_2HF_5 are consumed for the production of HF. Due to this, CO is not fully consumed around the second HRR peak (x = 4.5 – 6.0 cm) due to the lack of OH radicals which is essential for the oxidation of CO. In addition, because the mole fraction of C_2F_6 gradually decreases and the mole fractions of CF_4 and CF_2O gradually increases, it is considered that heat release there is due to reactions of species which do not contain H atoms. Regarding the profile of CO, it is completely consumed in the condition of 100:0, while CO is consumed half in the case of 50:50. Here, it is understandable that CO is not fully consumed at 0:100.

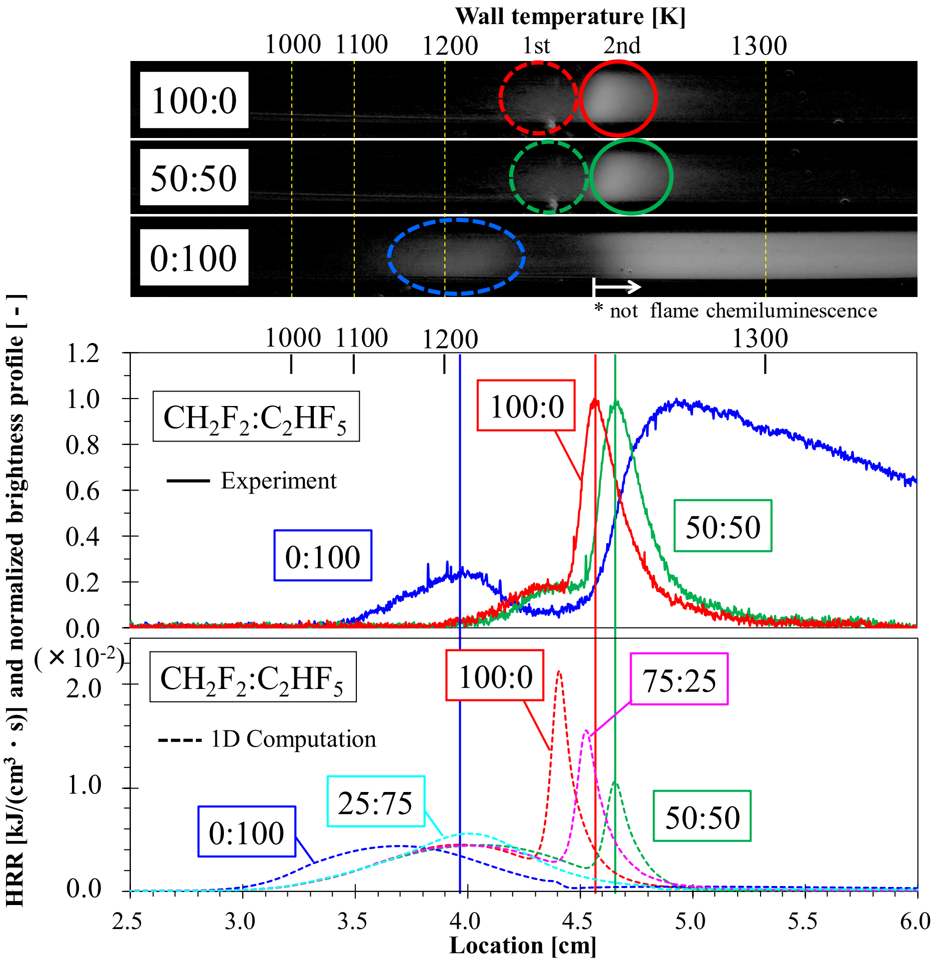

Fig. 2 Weak flame images, profiles of normalized brightness intensity and computational heat release rate (HRR) for 100:0, 50:50 and 0:100 (CH_2F_2:C_2HF_5). Computational HRR also showed the results on the condition of 75:25 and 25:75 as reference.

In the analysis of the flame structure, profiles of CO which is contributed to heat release were greatly different depending on the ratio of CH_2F_2 and C_2HF_5. In order to investigate the CO consumption in detail, rates of CO production at 100:0, 75:25, 50:50, 25:75 and 0:100 (CH_2F_2:C_2HF_5) are shown in Fig. 3(d). The positive value of the vertical axis indicates the production of CO and the negative value indicates the consumption of CO. In the case of 100:0, production of CO started around $x = 3.0$ cm and then turned to consumption around $x = 4.4$ cm. Similarly at 50:50, production of CO started at $x = 3.0$ cm and the maximum consumption rate was attained at $x = 4.7$ cm. In this case of 50:50, however, it is found that the position which shows the maximum consumption rate shifts to the high temperature side and the consumption rate is lower than the case of 100:0 and 75:25. From this trend, it was shown that consumption rate of CO decreases due to the increase of C_2HF_5 in the case of 100:0 to 50:50 and the consumption reaction occurs on the higher temperature side. This is considered to be due to the decrease of OH radicals required for CO consumption, because H radicals are consumed by HF formation at the first HRR peak. Generally, since OH radicals are mainly produced by H radicals, the amount of H radicals greatly affects the consumption of CO. Consumption of CO was mainly caused by the reaction of CO + OH = CO_2 + H which has the most largest contribution for second HRR peak [9]. It was shown that the lack of OH radicals causes a delay in the oxidation of CO because H radicals were extremely reduced in higher C_2HF_5 ratios. In the case of 25:75 and 0:100, most of the H radical is consumed at the first HRR peak, and consumption of CO hardly proceeds due to the lack of H. Based on the above, when the proportion of C_2HF_5 increases, that is, the ratio of F to H in the refrigerant increases, the consumption rate of CO decreases and CO consumption required higher temperature. Therefore, it is considered that the second HRR peak shifted to the higher temperature side. As a result, the second HRR peak at 50:50 shifts to the higher temperature side compared to 100:0 and the HRR peak also decreases because the CO consumption is not completed. The second HRR peaks in the case of 25:75 and 0:100 disappear because the consumption of CO which contributes to the second HRR peak hardly occurs.

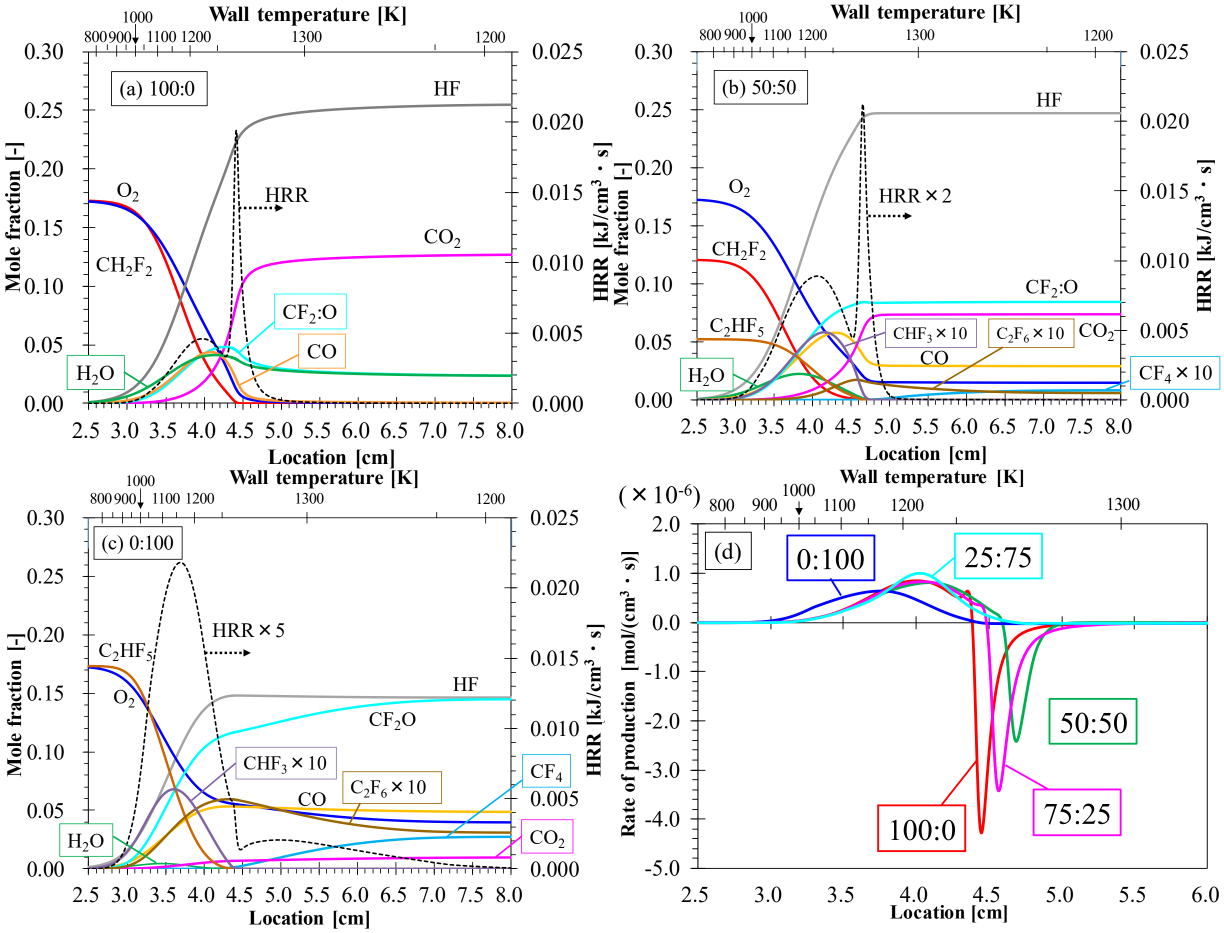

Fig. 3 Weak flame structure of (a) 100:0, (b) 50:50 and (c) 0:100, and (d) rate of CO production for 100:0, 75:25, 50:50, 25:75 and 0:100 (CH_2F_2:C_2HF_5).

4 Conclusions

Experiments and computations were conducted for weak flames of CH_2F_2,C_2HF_5 and mixed refrigerant in a micro flow reactor with a controlled temperature profile and the following conclusions were obtained.

For a mixed refrigerant (R410A, 50:50) and pure refrigerants (100:0, 0:100), Linteris mechanism qualitatively reproduced the experimental results.

From experiments and computations, it was found that position of the weak flames shifted to the high temperature side as the proportion of C_2HF_5 in the mixed refrigerant increase up to 50 wt%. When the proportion of C_2HF_5 exceeds 50 wt%, weak flame position shifted to the low temperature with the increase of C_2HF_5.

Analysis of flame structure and CO production rate of 100:0, 50:50 and 0:100 (CH_2F_2:C_2HF_5) revealed that unreacted CO increased with the addition of C_2HF_5 and contributes greatly to the heat release at high temperature region. This reduction of CO consumption rate is due to H radical reduction by HF formation at lower temperature region.

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