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Clarification of the disproportionation reaction of HFO-1123 and evaluation of the reaction inhibitor

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Abstract

The hydrofluoroolefin (HFO) refrigerant 1,1,2-trifluoroethene (HFO-1123) has a very low global warming potential (GWP) and ozone depletion potential (ODP); thus, it is proposed as a next-generation refrigerant. However, a short circuit of the motor under high-temperature and high-pressure conditions may cause a disproportionation reaction of HFO-1123. Therefore, to enable commercialization of HFO-1123 in split air conditioners, it is necessary to develop a technology to suppress the disproportionation reaction. In this study, disproportionation experiments were performed under various temperature and pressure conditions and changes due to these different pressure, temperature, and input energy were recorded. Conventionally, fusing and discharge methods are employed for ignition in experiments. Using the two ignition methods, we experimentally determined the threshold pressure of the disproportionation reaction and compared the differences in the reaction limits of the ignition methods. The disproportionation reaction was photographed with a high-speed camera, and the flame temperature was measured using the two-color temperature radiometry method (H & B method). The experiment was performed using difluoromethane (R32) and trifluoriodomethane (R131I) as disproportionation reaction inhibitors, and the suppression effect of the disproportionation reaction was evaluated.

Keywords: Refrigeration; HFO-1123; Reaction inhibitor; Disproportionation reaction.;

1. Introduction

In the fields of refrigeration and air conditioning, the development of alternative refrigerants such as hydrofluorocarbons (HFCs) has been promoted to prevent the depletion of the stratospheric ozone layer by chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) refrigerants. However, although the HFC refrigerant has a low ozone depletion potential (ODP), it has been regulated by the Global Change Framework Convention as a causative material for global warming due to its high global warming potential (GWP). Later, the Kigali amendment to the Montreal Protocol calling for the phase-down of HFC refrigerants was adopted in 2016; subsequently, UN member states were required to switch to low-GWP refrigerants, such as hydrofluoroolefins (HFOs) and natural refrigerants.

Trifluoroethene (HFO-1123, CF_2CHF) has a very low GWP, as shown in Table 1, because it has a short lifespan in the atmosphere. Therefore, it is expected to be a next-generation refrigerant in the fields of refrigeration and air conditioning. However, HFO-1123 is known to cause a disproportionation reaction under high-temperature and high-pressure conditions, as shown in Eq. (1). When energy is applied due to equipment failure, the generated flame propagates, and the pressure and temperature may increase significantly due to the generated heat. This is not a combustion reaction that requires oxygen, but a self-decomposition reaction.

Table 1. GWP and ODP of typical refrigerants (HFC-410A, HFC-32, and HFO-1123)

	HFC-410A	HFC-32	HFO-1123
ODP	0	0	0
GWP	2090	675	0.3



To put HFO-1123 to practical use, it is necessary to clarify the conditions under which the disproportionation reaction occurs and to suppress the reaction because the occurrence of a disproportionation reaction is dangerous. It is also effective to add a reaction inhibitor. There are two possible mechanisms for inhibiting the disproportionation reaction of HFO-1123 by the addition of substances.

- (1) The thermal dilution effect of mixing inactive gases.
- (2) The suppression of disproportionation reaction propagation by trapping radicals of the reaction intermediate products.

In this study, the conditions for the disproportionation reaction were investigated experimentally for the composition of HFO-1123 mixed with two types of inhibitors, as shown in the triangular diagram in Fig. 1. Table 2 summarizes the test gas composition, where R32 stands for difluoromethane and R131I denotes trifluoroiodomethane. The mixed composition of R32 was selected such that the GWP of the gas mixtures was 150 or 200. The initial temperature of the test gas was fixed at 150 °C, and the initial pressure was changed to determine whether the disproportionation reaction propagated. When the initial pressure is low, the flame does not propagate, but when it exceeds a certain pressure, it propagates. As the pressure increases and the density of the HFO-1123 molecules increases, the reaction continues, and the flame propagates. The pressure at the boundary where the flame propagates was examined. To investigate the mechanism of the reaction inhibitor, the flame temperature was measured, and a qualitative analysis of the reaction gas was performed using gas chromatography–mass spectrometry (GC–MS).

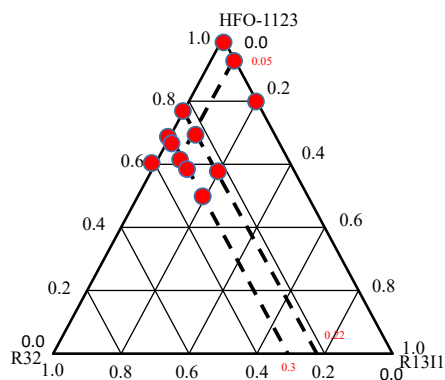


Fig. 1. Ternary plot of the compositions of the test gas mixtures

Table 2. Compositions of the test gas mixtures

No.	GWP of mixture	HFO-1123 (mass%)	R32 (mass%)	R131I (mass%)
1-1		100		0
1-2	< 10	95	0	5
1-3		80		20
2-1		78		0
2-2	150	72.4	22	5.6
2-3		58		20
3-1		70		0
3-2		68		2
3-3	200	65	30	5
3-4		60		10
3-5		50		20
4-1	270	60	40	0

2. Experimental method

Figure 2 shows the experimental apparatus used for observing the disproportionation reaction of HFO-1123 and for investigating the pressure boundary where the disproportionation reaction was propagated. The experimental equipment consists of a stainless-steel pressure vessel, an ignition source, a vacuum pump, a refrigerant vessel, and a safety valve. After the pressure and temperature of the gas supplied to the pressure vessel were set at certain values and stabilized, energy was applied, and the disproportionation reaction was initiated. Subsequently, it was determined from the pressure change whether the reaction propagated or not. At the same time, the movement of the flame was observed from the two upper and lower observation windows installed in the pressure vessel.

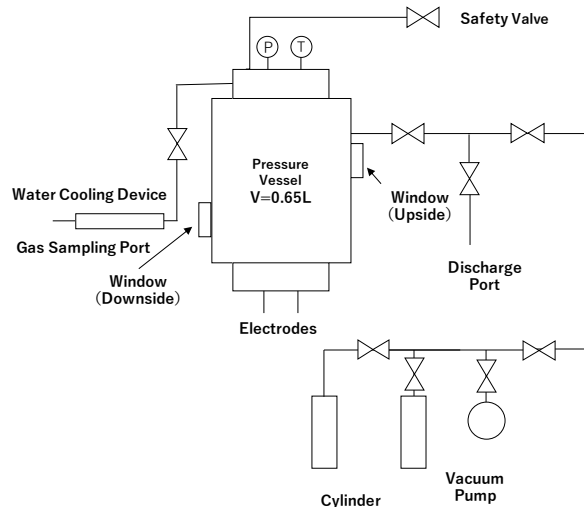


Fig. 2. Outline of the experimental apparatus

In previous studies, energy was introduced into the pressure vessel by fusing thin molybdenum wires; however, in this study, we switched to the arc discharge method. This is because the arc discharge is similar to a short circuit that may occur in the compressor motor of air conditioners. The arc discharge is a continuous large current generated between the electrodes at a low voltage, unlike a spark discharge, which is a discontinuous discharge generated between the electrodes at a high voltage.

In this experiment, a part of two copper spiral electrodes partially overlapped, and a 220 V DC was applied between the electrodes for 1.5 ms to generate an arc discharge between the spiral electrodes, and energy was supplied into the pressure vessel. The input energy was calculated from the results of the time-integrated changes in the voltage and current.

Figure 3 shows the current–voltage (I–V) curve of an ideal discharge that occurs in air. Because the high insulation resistance of the refrigerant gas hindered the discharge, the I–V curve is as shown in Fig. 4. The input energy during the discharge in air was in the range of 16–18 J, and it was in the range of 20–24 J during the discharge in the refrigerant after heating.

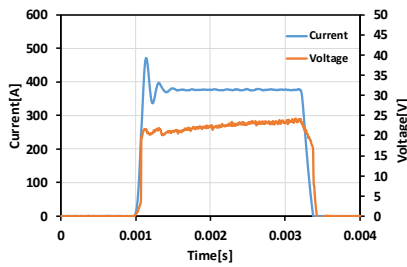


Fig. 3. I–V curve of the ideal discharge in air

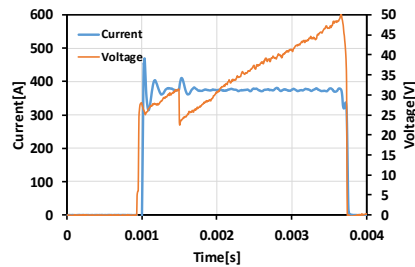


Fig. 4. I–V curve of the discharge in refrigerant

3. Experimental results

3.1 Ignition by fusing method

When the fusing method was employed for ignition, it was determined that the disproportionation reaction had propagated when a large pressure increase was measured; when the pressure increase was not measured, it was determined that the disproportionation reaction did not propagate. Figure 5 shows the results of the pressure boundary where the reaction propagates when the gas temperatures before the reaction were 100, 130, 150, and 170 °C. Although the disproportionation reaction was considered to propagate at a pressure above the solid line in Fig. 5, the boundary was stochastic and not deterministic.

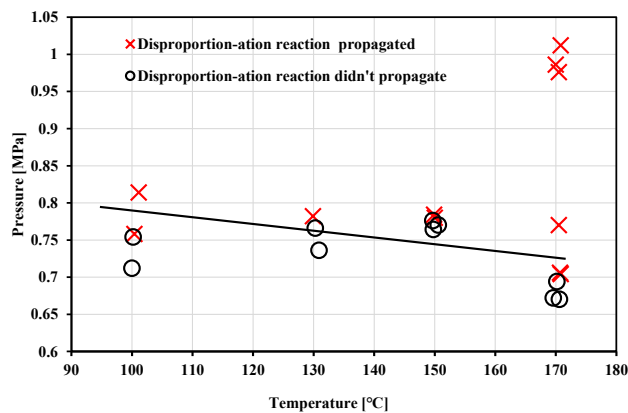


Fig. 5. Result of disproportionation reaction of HFO-1123 by fusing method

3.2 Ignition by discharge method

Compared with the fusing method, the discharge method could not easily determine whether the disproportionation reaction propagated as a result of the increase in pressure. In some cases, the pressure did

not increase even when a flame was observed, and the relationship between the flame propagation and pressure increase was unclear. In this study, we considered two criteria for determining the propagation of the disproportionation reaction of HFO-1123.

Judgment condition (1): When there is a sharp peak in the pressure change, as shown in Fig. 6, it is determined that the disproportionation reaction has propagated. If this condition is not satisfied, it is determined that the disproportionation reaction has not propagated even if a flame is observed from the observation window.

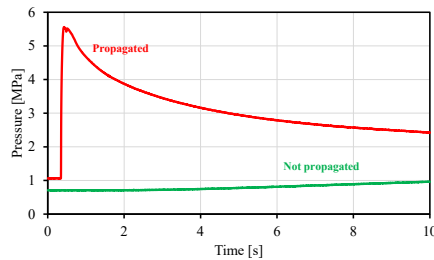


Fig. 6. Examples of the propagated and not propagated cases using judgment condition (1)

Judgment condition (2): Determine whether the reaction has propagated based on the pressure convergence value 10 s after ignition. When the pressure after 10 s exceeds the initial pressure by 1.5 times, it is determined that the disproportionation reaction has propagated.

Based on the judgment conditions described above, the pressure boundary at which the disproportionation reaction of HFO-1123 and gas mixtures propagate at a temperature of 150 °C was investigated.

3.3 Pure refrigerant HFO-1123

For the HFO-1123 refrigerant, the pressure boundary at which the disproportionation reaction propagated was investigated experimentally while maintaining a temperature of 150 °C. The pressure boundary was investigated based on the two judgment conditions described in Section 3.2. Figure 7 shows the pressure change after the voltage application. By observing the pressure change, it was found that the pressure waveform was divided into two cases: a sudden increase and a gradual increase. Even when the disproportionation reaction was considered not to have propagated when the fusing method was used (e.g., 150 °C and 0.70–0.76 MPa), an increase in the pressure was observed in the discharge method.

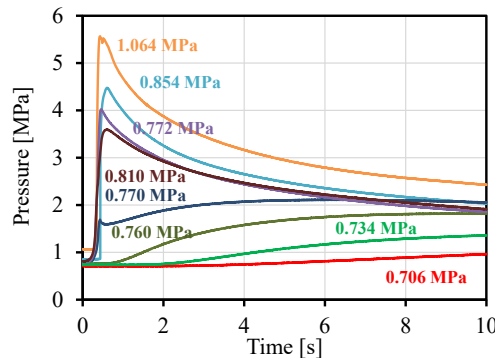


Fig. 7. Pressure curve of HFO-1123 after ignition

Figures 8 and 9 show the results of comparing the pressure boundary using the two judgment conditions and the pressure boundary using the fusing method. Based on the results of judgment condition 1, when the initial pressure is 0.772 MPa, the pressure increases stochastically with a peak, and when the initial pressure is 0.770 MPa, it increases stochastically gradually. The pressure condition at which the reaction propagated

was approximately 0.770 MPa. This is close to 0.780 MPa, which is the pressure boundary of the fusing method. Conversely, using judgment condition 2, the pressure boundary was approximately 0.75 MPa, which was slightly different from that of the fusing method. From the perspective of risk assessment, it is possible to prevent accidents due to compressor explosions by utilizing a pressure-relief valve if the pressure increases slowly. Hence, we considered that the speed of the pressure increase was more significant than the converging pressure and decided to use only judgment condition 1 to determine the pressure boundary.

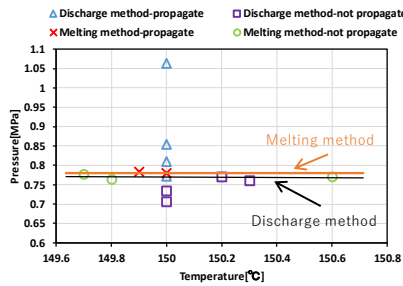


Fig. 8. Result using judgment condition (1)

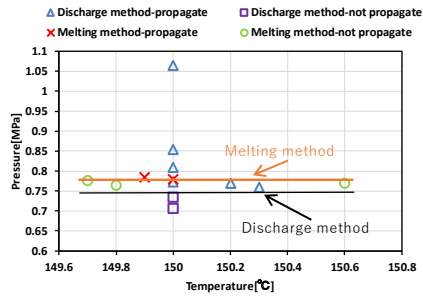


Fig. 9. Result using judgment condition (2)

3.4 Binary mixtures of HFO-1123 + R32 or R131I

Experiments to determine the pressure boundary of the disproportionation reaction of gas mixtures containing HFO-1123, R32, and R131I were conducted using the discharge method at an initial temperature of 150 °C.

(1) Binary mixtures of HFO-1123 + R32

Mixing the R32 refrigerant with HFO-1123 is expected to lower the partial pressure of HFO-1123 and dilute the heat of the disproportionation reaction. The GWP of the mixed gases was set to 150 and 200 by mixing 22 mass% and 30 mass% of R32 (GWP 675), respectively. The test mixtures of HFO-1123 + R32 were named No. 2-1, No. 3-1, and No. 4-1 (Table 2).

Figure 10 shows the relationship between the initial pressure and the pressure increase of No. 2-1. The pressure boundary is between 0.82 and 1.05 MPa. When the concentration of R32 is 30 mass%, as shown in Figure 11, the pressure boundary of No. 3-1 is 1.54 MPa. When the concentration of R32 is increased to 40 mass% (No. 4-1), the pressure boundary is considered to be over 2.0 MPa.

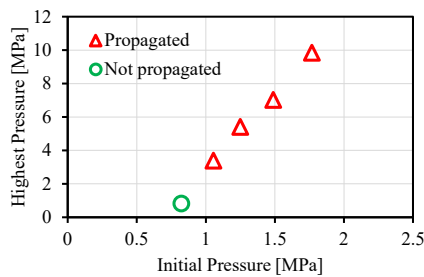


Fig. 10. Judgment map of reaction propagation for the gas mixture of HFO-1123 + 22 mass% R32 (No. 2-1)

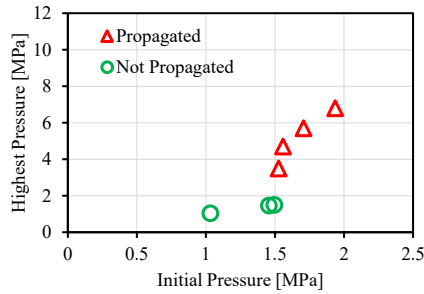


Fig. 11. Judgment map of reaction propagation for the gas mixture of HFO-1123 + 30 mass% R32 (No. 3-1)

(2) Binary mixtures of HFO-1123 + R131I

R131I is a typical flame retardant and is often used as a fire extinguisher. It is also used in the non-flammable refrigerant R466A, developed by Honeywell. It is expected that iodine in the R131I molecule will trap the radicals generated during the disproportionation reaction. Because a small amount of addition is expected to have an inhibitory effect, mixed compositions of 5 and 20 mass% were used. The pressure boundary of the No. 1-2 results is shown in Fig. 12. The results show that when R131I is mixed at 5 mass%, the pressure boundary is approximately 0.92 MPa, and there is no dramatic reaction suppression effect. When the concentration of R131I was increased to 20%, as shown in Fig. 13, the pressure boundary of No. 1-3 decreased instead.

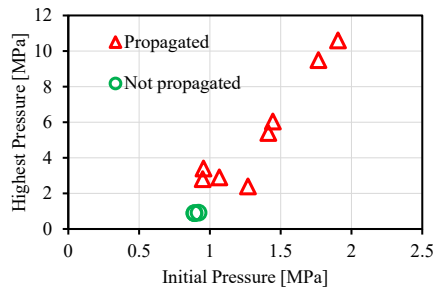


Fig. 12. Judgment map of reaction propagation for the gas mixture of HFO-1123 + 5 mass% R131I (No. 1-2)

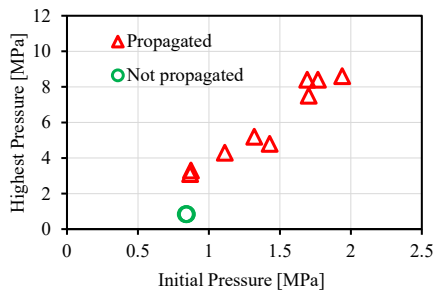


Fig. 13. Judgment map of reaction propagation for the gas mixture of HFO-1123 + 20 mass% R131I (No. 1-3)

3.5 Ternary mixtures of HFO-1123 + R32 + R131I

As a result of the experiments with binary gas mixtures, in which R32 or R131I was mixed with HFO-1123, the suppression effect was not as great as expected. Therefore, experiments were conducted with ternary gas mixtures in which two types of inhibitors were mixed simultaneously. Figure 14 shows the results of the determination of gas mixture No. 3-3. The pressure boundary was between 1.54 MPa and 1.61 MPa. These results indicate that a synergistic effect can be obtained when the inhibitors with two types of inhibition mechanisms are mixed at the same time. In Fig. 15, when the concentration of R32 was 30 mass%, the pressure boundary increased to 2.36 MPa.

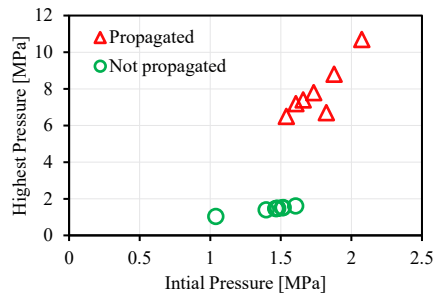


Fig. 14. Judgment map of reaction propagation for the gas mixture of HFO-1123 + 5.6 mass% R131I + 22 mass% R32 (No. 2-2)

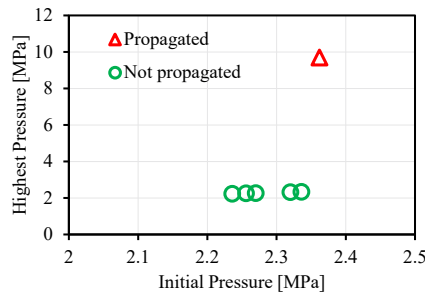


Fig. 15. Judgment map of reaction propagation for the gas mixture of HFO-1123 + 5 mass% R131I + 30 mass% R32 (No. 3-3)

3.6 Flame temperature measurement by the two-color method

Flame temperature is an important parameter when analyzing combustion phenomena using a thermal model. The disproportionation reaction is similar to the combustion reaction from the viewpoint of flame propagation. Thus, it would be beneficial to measure the flame temperature. Therefore, in this study, the flames caused by the disproportionation reaction were photographed with a high-speed camera from two observation windows installed at the top and bottom of the pressure vessel, and the flame temperature was analyzed using the two-color method. The flame of HFO-1123 taken from the upper window is shown in Fig. 16. The generated soot appears black, and the flame shines brightly. The shooting speed is 3000 f/s, and the exposure time is 100 μ s.

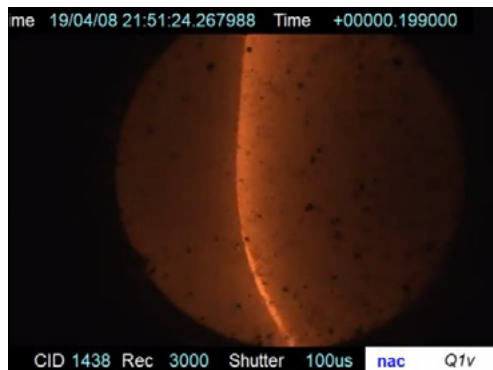
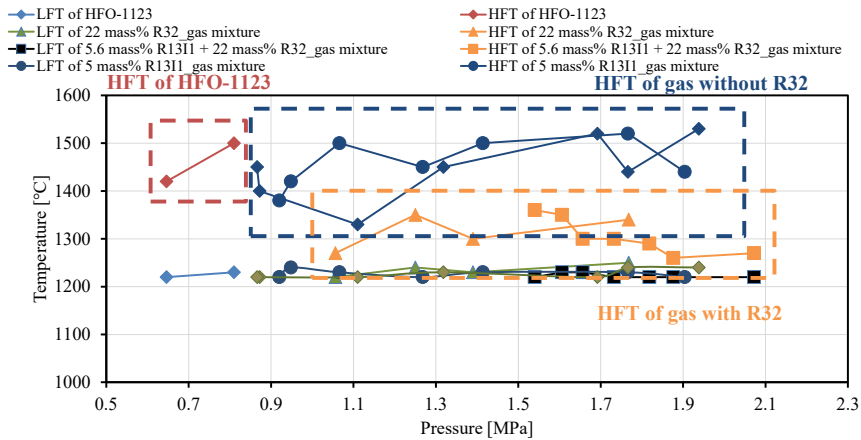


Fig. 16. Flame of HFO-1123

The flame temperature varies with a large distribution in place and time. In this study, the mode temperature of the flame was defined as the flame temperature, and the maximum and minimum values were analyzed. The results for pure HFO-1123 and the three types of gas mixtures are shown in Fig. 17.

The results of the flame temperature measurement show that the minimum flame temperature remains almost unchanged between 1200 and 1250 °C; however, the maximum flame temperature is divided into two groups, depending on whether or not R32 is included in the mixture. The maximum flame temperatures of HFO-1123 and the HFO-1123 + R131I mixture were 1400–1500 °C, whereas the maximum flame temperatures of the gas mixed with R32 were 1250–1350 °C. It is assumed that the decrease in the maximum flame temperature results from the thermal dilution effect of R32.



LFT: Lowest Flame Temperature HFT: Highest Flame Temperature

Fig. 17. Results of flame temperature analysis of the test gas mixtures

3.7 Qualitative analysis of the disproportionated reaction gas by GC-MS

In this study, when the disproportionation reaction propagated, the reaction gas was collected after water cooling, and a qualitative analysis of the gas composition was performed using GC-MS. Fig. 18 shows the composition analysis results of the reaction gas of HFO-1123. The reaction gas composition of the 22 mass% R32 gas mixture was almost the same as that of HFO-1123.

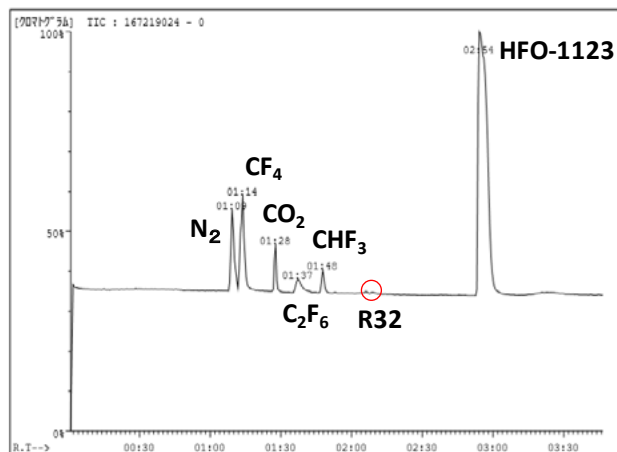


Fig. 18. Results of qualitative analysis of reaction gas of HFO-1123

The results of the qualitative analysis of the 5.6 mass% R131I + 22 mass% R32 + 72.4 mass% HFO-1123 gas mixture are shown in Fig. 19. A plurality of intermediate products could be detected in the reaction gas. This is presumed to be the result of the change in the disproportionation pathway caused by R131I.

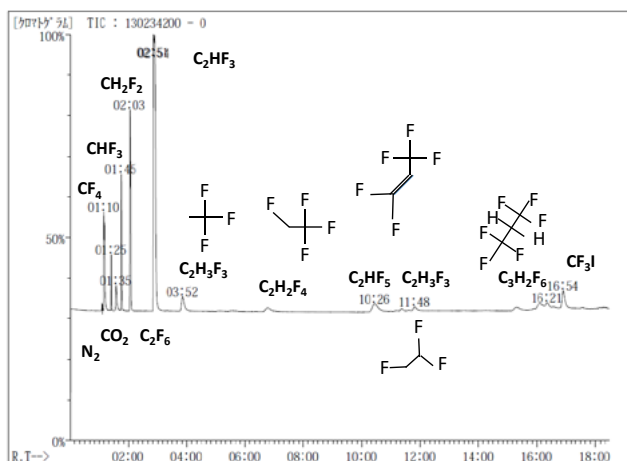


Fig. 19. Results of qualitative analysis of reaction gas of 5.6 mass% R1311 + 22 mass% R32 + 72.4 mass% HFO-1123 mixture

4. Conclusion

In this study, the initial temperature was fixed at 150 °C, and the boundary was investigated of the initial pressure at which the disproportionation reaction of HFO-1123 and the gas mixtures was propagated. The pressure boundary of each gas mixture is illustrated in Fig. 20. The pressure boundary increased from 0.77 MPa to over 2.0 MPa by mixing with 40 mass% R32, which is expected to be suppressed by thermal dilution, and the pressure boundary increased to 0.92 MPa by mixing with 5 mass% R1311, which is expected to be suppressed by radical trapping. The suppression effect of mixing only one type of inhibitor was not significant. However, in the case of the ternary gas mixed with inhibitors having two types of inhibition mechanisms simultaneously, an enhanced suppression effect could be obtained, and the pressure boundary increased to over 2.4 MPa (No. 3-5). In addition, to evaluate the suppression effect, the maximum and minimum values of the mode temperature of the flame were obtained using the two-color method, and the composition analysis of the reaction gas was also investigated using GC-MS. Consequently, it was found that R32 exerts a thermal dilution effect and R1311 changes the reaction pathway.

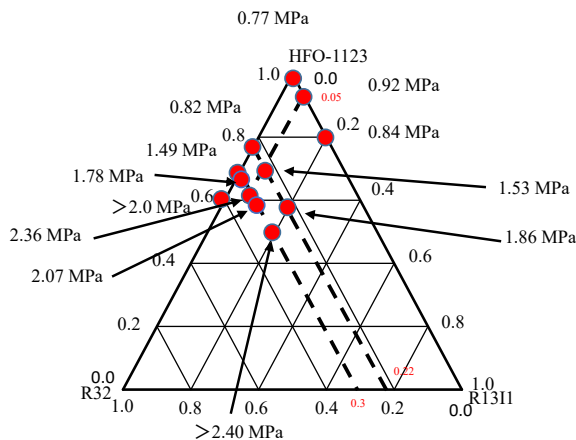


Fig. 20. Pressure boundary of each of the gas mixtures

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