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Disproportionation Reaction of HFO-1123 Refrigerant

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ABSTRACT

In the field of refrigeration and air conditioning, the transition from using chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) to using hydrofluorocarbon (HFC) as refrigerants has been driven by the need to prevent the depletion of the stratospheric ozone layer. Although HFC refrigerants have low ozone depletion potential, their high global warming potential (GWP) is a serious concern. After the passing of the Kigali Amendment to the Montreal Protocol, UN member nations are now required to switch to low-GWP refrigerants, such as hydrofluoroolefins (HFO), and natural refrigerants. HFO-1123 has very low GWP and should emerge as a new refrigerant in refrigeration and air-conditioning equipment. However, HFO-1123 may undergo a disproportionation reaction under high-temperature and high-pressure conditions. This is a self-decomposition reaction accompanied by significant increases in pressure and temperature. Therefore, to put HFO-1123 into practical use, it is first necessary to develop technology to suppress the disproportionation reaction. The conditions favoring disproportionation of HFO-1123 are influenced by the temperature and pressure of the reaction gas as well as by the activation energy. This reaction can be suppressed by mixing other substances with the refrigerant. In this study, we investigated the effects of mixed substances of varying constituents and concentrations on the suppression of disproportionation at various temperatures and pressures. Using a metallic pressure vessel having a volume of 0.65 L, energy was input by adding molten molybdenum to pure HFO-1123 and to a mixture containing HFO-1123 and other substances under various temperature and pressure conditions. The changes in the pressure and temperature were then measured. Based on the obtained experimental data, the effects of the mixed substances on the reaction were evaluated. Then, a model to estimate the occurrence of disproportionation reactions of HFO-1123 was proposed. The validity of the model was examined using the experimental results.

1. INTRODUCTION

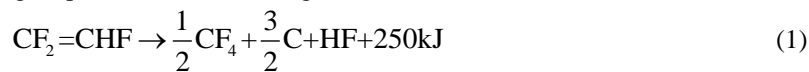
Since the Montreal Protocol entered into force in 1987, a shift from chlorofluorocarbon (CFC) or hydrochlorofluorocarbon (HCFC) to hydrofluorocarbon (HFC) has proceeded in the field of refrigeration and air conditioning to prevent destruction of the ozone layer. HFC refrigerant has no ozone depletion potential (ODP) and is useful from the viewpoint of protection of the ozone layer; however, its high global warming potential (GWP) is a major disadvantage. Recovery of the refrigerant used in refrigeration air conditioning equipment is mandatory, but the recovery rate is low. Thus, for preventing global warming, all UN member nations are now required to switch from conventional to lower GWP refrigerants, under the Kigali amendment to the Montreal Protocol. A substance that is easily decomposed in the atmosphere and has a short life time has small GWP; however, this means that its reactivity in the atmosphere is high. Therefore, in many cases, compounds expected to emerge as new low-GWP refrigerants have the disadvantage of relatively higher reactivities than conventional ones. Moreover, these compounds are highly flammable and may undergo self-decomposition reaction. The instability of refrigerants becomes a problem in the conversion to low-GWP substances; thus, it is necessary to evaluate their risks.

HFO-1123 ($\text{CF}_2=\text{CHF}$) is a hydrofluoroolefin (HFO) containing no chlorine in the molecule, and thus, does not present the concern of destroying the ozone layer. Since HFO has a carbon-carbon double bond, it has low chemical stability and short atmospheric lifetime. Therefore, HFO-1123 has much smaller GWP than the HFC refrigerants HFC-410A and HFC-32 currently used in household air conditioners.

Table 1. Properties of typical refrigerants

	HFC-410A	HFC-32	HFO-1123
ODP	0	0	0.0
GWP	2090	675	0.3

HFO-1123 is expected to be a next-generation refrigerant for air conditioners. However, it is known to undergo self-decomposition by disproportionation upon addition of energy under high-pressure and high-temperature conditions, even without an oxidizing agent such as oxygen (Lisochkin and Poznyak, 2006). This reaction, represented by Equation (1), is rapid, violent, exothermic, accompanied by a rapid pressure rise. Thus, it poses a danger that cannot be ignored considering its practical use as a refrigerant for air conditioners.



The disproportionation of HFO-1123 occurs even in the absence of oxygen, and it also produces substantial amounts of heat. Since the reaction proceeds only in high temperatures and high pressures, it will not occur as a result of a leakage of the refrigerant from an air conditioner into the room. However, if a layer short circuit occurs inside the motor of the compressor, and discharge energy above a certain value is supplied, disproportionation of HFO-1123 may proceed inside the compressor.

In an accident scenario that could occur when HFO-1123 is used as a refrigerant in a constant-speed air conditioner, the following causes should be considered. First of all, a human error in forgetting to open the three-way valve when installing the air conditioner; the heating operation is then started in a state in which the compressor and the safety device of the control unit do not work. Consequently, after repeating intermittent operations, the compressor is always energized due to electric circuit failure which causes its temperature to rise. After that, the contact short circuit of the overcurrent circuit breaker overlaps and the breaker does not function anymore as a protection device; the motor part generates heat due to the overcurrent, the temperature rises and damages the insulation of the motor winding. High energy, such as current spark, is generated and triggers disproportionation of HFO-1123. According to previous studies, it was found that the disproportionation of HFO-1123 was suppressed by mixing the R32 refrigerant with HFO-1123 (Otsuka *et al.*, 2018). In this research, we aimed to commercialize HFO-1123 as a refrigerant in air-conditioning equipment, and we studied its disproportionation reaction, which presents an obstacle for this purpose. Experiments were conducted, using a metal pressure vessel, to study the effect of admixing substances to HFO-1123 on suppressing the disproportionation reaction.

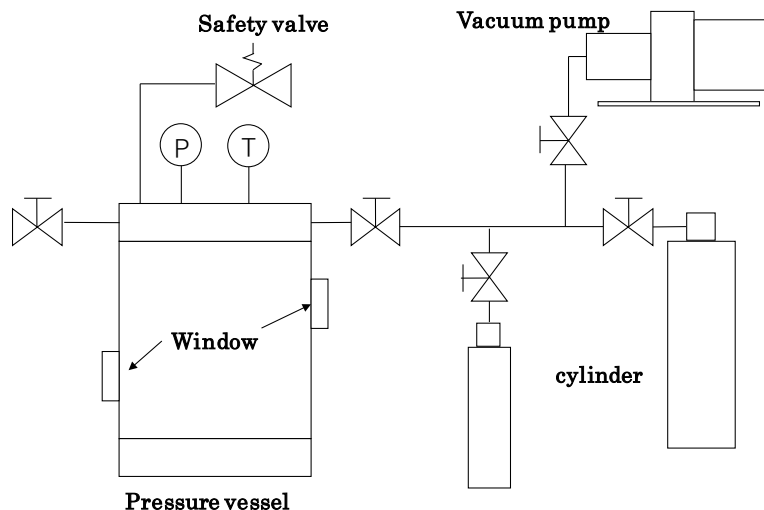


Fig. 1. Outline of the experimental apparatus.

2. EXPERIMENTAL METHOD

2.1 Outline of the experiment

The experimental apparatus to observe the disproportionation reaction of HFO-1123 and to investigate the reaction conditions in series of experiments, is shown in Fig. 1. It consists of a stainless steel pressure vessel, a vacuum pump, a refrigerant container, a pipe for introducing and discharging the refrigerant, a valve, and a safety valve. HFO-1123 and other substances, such as propane, as the reaction inhibitors were introduced into the pressure vessel, and the temperature and pressure were changed. Then, as the disproportionation reaction was initiated, it was observed whether it propagated or not.

2.2 Experimental apparatus

The refrigerant was introduced into a stainless steel vessel (Fig. 2) having a pressure resistance of 29 MPa and a temperature resistance of 200 °C. The inside of the vessel was cylindrical with a diameter of 75 mm and a height of 148 mm; the internal volume of the vessel was 0.65 L. To observe the reaction, there were two circular quartz glass windows with diameter of 20 mm, on the side of the vessel at heights of 54 mm and 94 mm from the bottom of the interior of the vessel. Four 300-W cartridge heaters were inserted in the side wall of the vessel to control the gas temperature inside the vessel and the temperature of the vessel itself, between ambient temperature and 200 °C. Two round copper electrodes with diameters of 3 mm, spaced 45 mm apart, were inserted into the vessel at a height of 40 mm from the bottom of the inside the vessel in order to input energy to the gas inside.



Fig. 2. The pressure vessel.



Fig. 3. The electrodes.

2.3 Discharged energy

In this experiment, energy input at the start of the experiment was carried out by melting a Mo metal wire. The Pt wire fusing method was not used because Pt, unlike Mo, may exhibit a catalytic effect on the reaction. By connecting the copper electrodes with the molybdenum wire in the vessel and applying a high voltage with a power supply device, the molybdenum wire was heated and melted, supplying the activation energy necessary for initiation of the disproportionation reaction.

Fig. 4 summarizes the relationship between the molybdenum wire diameter, its length, and the input energy. By increasing the molybdenum wire diameter, the fusion energy input increased; an increase in the length of the wire caused a similar increase in input energy. The results showed that the energy to be charged can be controlled within the 5–200-J range by adjusting the diameter and length of the molybdenum wire. Figure 5 shows the temporal changes in the current and voltage when the molybdenum wire melts. Voltage application started at 100 ms after the measurement began. Looking at the time variation of the current, the current sharply increased when the voltage was applied, and shortly thereafter it smoothly decreased until 105 ms. This was because of a rise in the temperature and the resistance of the molybdenum wire due to the heat generated by the current flowing through it. The current sharply dropped after 105 ms, and it was estimated that melting of the molybdenum wire occurred at this time. It was confirmed that the voltage value was stable at 100 V.

The amount of energy input by melting the molybdenum wire was calculated by integrating the product of current and voltage over time.

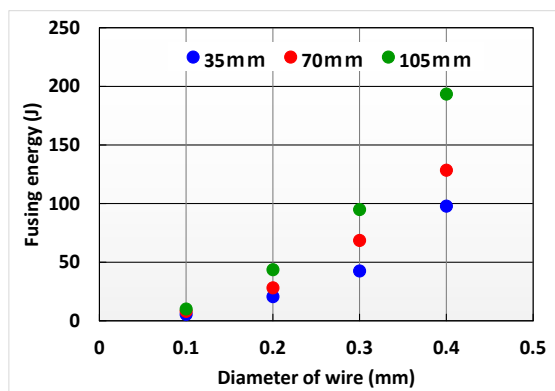


Fig. 4. Relationship between the molybdenum wire diameter, length and fusion energy.

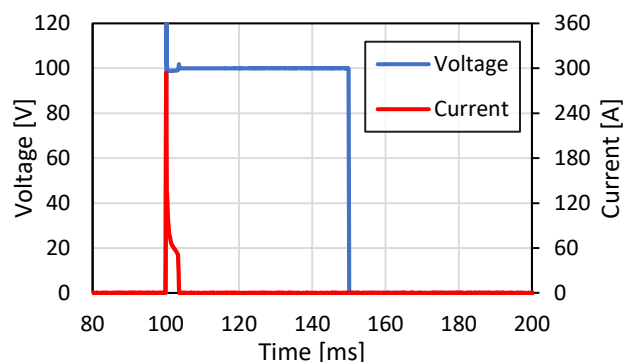


Fig. 5. Time change of the voltage and current.

2.4 Experimental procedure

The experiments were carried out following the procedure described below:

- 1) Vacuumizing the vessel and the piping for 10 min.
- 2) Introducing the HFO-1123 and the admix-gas into the vessel at room temperature while monitoring the pressure.
- 3) Raising the temperature inside the vessel up to the target temperature.
- 4) Inputting energy by melting the molybdenum wire while measuring the pressure and temperature change inside the vessel, and the current and the voltage in the electrode part.
- 5) Discharging the gas from the vessel and inspecting the interior of the vessel.

2.5 Experimental conditions

To clarify the influence of pressure and temperature at the energy input time on propagation of the HFO-1123 disproportionation reaction, experiments, which conditions are presented in Table 2, were carried out.

Table 2. The experimental conditions.

Volume of the vessel	0.65 L
Diameter of the molybdenum wire	0.2 mm
Length of the molybdenum wire	60 mm
Voltage	100 V
Operation time	0.1 s
Gas temperature	100-200 °C
Gas pressure	0.60–0.85 MPa
Input energy	26.60–30.51 J

3. HFO-1123 DISPROPORTIONATION EXPERIMENT

3.1 Propagation of the disproportionation reaction

The preliminary experiments to investigate the reaction were conducted under the conditions given in Table 3: No. 1 was a condition under which the reaction does not propagate, while No. 2 was a condition favoring disproportionation.

Table 3. The conditions of the preliminary experiments.

No.	Temperature (°C)	Pressure (MPa)	Energy input (J)
1	200	0.608	30.51
2	200	0.753	29.38

Figs. 6 and 7 show time variations of the pressure, temperature, and current in the conditions No. 1 and 2, respectively. Application of electricity to the electrode began after 100 ms from the start of the measurement; at the same time started the energy input to the gas in the pressure vessel. In both cases, the voltage application was continued for 100 ms, although it was confirmed, basing on the current waveform, that the molybdenum wire melted within approximately 5 ms after the electricity application, and thereafter no further current flow was detected. In the case of the No. 1 conditions (Fig. 6), the temperature and pressure inside the vessel did not change after the energy input, and propagation of the disproportionation reaction could not be confirmed. On the other hand, under the No. 2 conditions (Fig. 7), the pressure increased to 3.7 MPa and the temperature to 600 °C after the electricity application. Additionally, a large amount of soot was produced near the electrodes in the pressure vessel under these conditions. All the above observations confirm the occurrence of the disproportionation that propagated to the entire vessel. Under the No. 1 conditions, only a very small amount of soot was produced, providing an extra proof that the disproportionation reaction did not propagate.

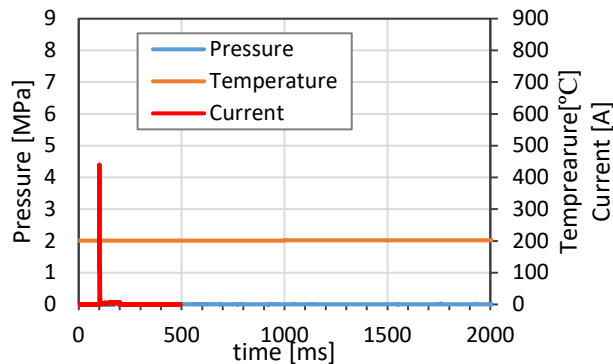


Fig. 6. Time variation of the pressure inside the vessel (200 °C, 0.608 MPa).

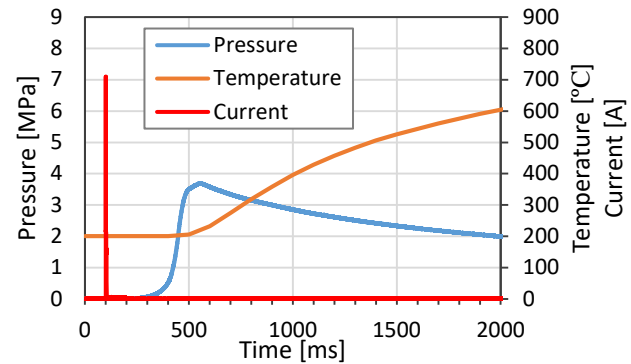


Fig. 7. Time variation of the pressure inside the vessel (200 °C, 0.753 MPa).

3.2 Effect of temperature and pressure on the disproportionation reaction

The propagation of disproportionation under various temperature and pressure conditions is shown in Fig. 9, in which the crosses represent the conditions under which the reaction proceeded; the circles, the conditions in which the reaction did not occur, and the solid line shows the boundary. It was confirmed that the disproportionation reaction tends to propagate as the pressure rises.



Fig. 8. Soot production during the disproportionation reaction.

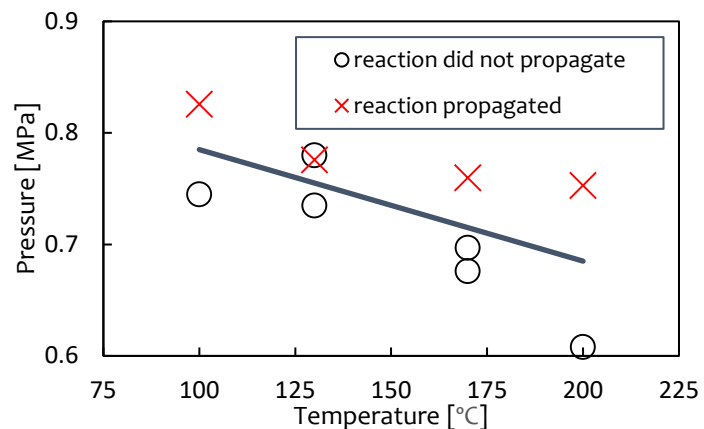


Fig. 9. The temperature and pressure effects on the HFO-1123 disproportionation reaction.

4. DISPROPORTIONATION REACTION EVALUATION BY THE COMBUSTION THEORY

If a theoretical model of propagation of the HFO-1123 disproportionation reaction is established, it will be very useful for searching for substances with high inhibitory effect on the reaction. Therefore, it was investigated whether propagation of the HFO-1123 disproportionation reaction can be described by existing combustion theory.

4.1 Combustion theory

In the combustion theory, there is a minimum ignition energy which is required to ignite a gas (E_{min}) and it is represented by Equation (2). The quenching distance (d_{min}) (Equation (3)) represents the lower limit of the flame size formed by the initial flame kernel created by the energy input, that can assure a sustainable flame propagation. Burning velocity is described by Equation (4)

$$E_{min} = \frac{1}{6} \pi d_{min}^3 \rho_u C_{p_u} (T_b - T_u) \quad (2)$$

$$d_{min} = 50.16 \frac{1}{(\rho_u S_u)^{0.847}} \quad (3)$$

$$S_u = \frac{1}{\rho_u} \sqrt{\frac{\lambda_u \omega}{C_{p_u}}} \quad (4)$$

Assuming that combustion is one global reaction, the reaction rate can be described by Equation (5).

$$\omega = D p^N \exp(-E/RT_b) \quad (5)$$

By substituting Equation (2) with Equations (3), (4) and (5), the minimum ignition energy can be expressed by Equation (6).

$$E_{min} = \frac{B}{\lambda^{1.2705} p^{1.2705N} \exp(-1.2705E/RT_b)} C_p^{2.2705} \rho_u (T_b - T_u) \quad (6)$$

4.2 Comparison between the combustion theory and the experiments

If the reaction order, N , is assumed, the relationship between temperature and pressure for a specific minimum ignition energy can be estimated by Equation (6). It was investigated whether the occurrence boundary of propagation of the disproportionation reaction can be expressed by Equation (6). The results of the experiment and the estimation are shown in Fig. 10.

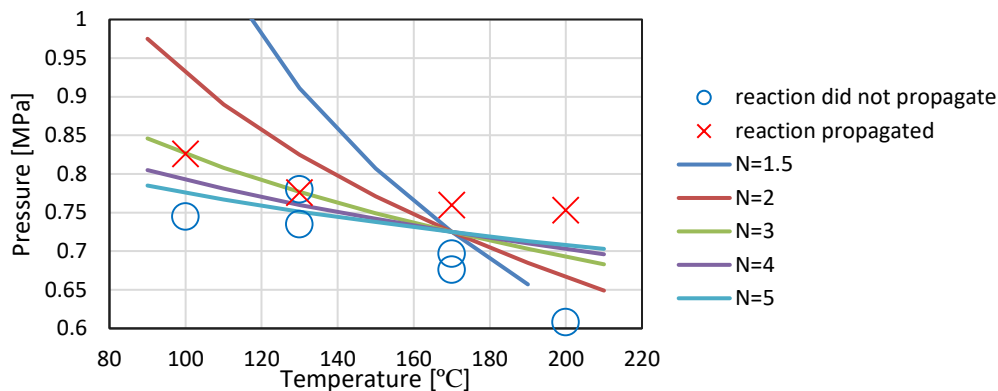


Fig. 10. The experimental results and the isoenergy curve changes depending on the reaction order (N).

The reaction order was varied from 1.5 to 5; the minimum ignition energy was found at 170 °C and 0.725 MPa assumed it to be the crossing point of the estimation curves at different N 's. The physical properties were calculated with NIST REFPROP Database, and the adiabatic flame temperature was assumed to be 2520 K. In this experiment, the parameters related to the input energy and the actually measured power have almost the same values. Therefore, the occurrence boundary of propagation of the disproportionation reaction in this experiment can be regarded as the boundary for a certain input energy. Based on the data presented in Fig. 10, it is expected that the combustion-based Equation (6) be also applicable to propagation of the disproportionation reaction because the boundary in the experiment can be expressed by assuming $N = 4$.

5. SUPPRESSION OF THE REACTION BY ADDITION OF INACTIVE SUBSTANCE

5.1 Results of the experiments

To, the effect of inactive substance addition on suppressing the disproportionation reaction was investigated. R32 refrigerant and propane were chosen as the inert substances. The experimental conditions and results are summarized in Table 4. The results for pure HFO-1123 were also included for comparison.

Table 4. Experimental conditions and results for the reference refrigerant and with admixtures of propane or R32.

No.	Additive gas	Mixed composition (wt%)	Temperature (°C)	Pressure (MPa)	Partial pressure of HFO-1123 (MPa)	Input energy (J)	Propagation
1	-	0.00	170	0.697	—	28.1	No
2	-	0.00	170	0.760	—	28.0	Yes
3	propane	2.75	170	0.950	0.903	28.8	No
4	propane	2.75	170	1.180	1.070	27.1	Yes
5	propane	20.00	170	1.130	0.771	29.2	No
6	propane	20.00	170	1.770	1.210	27.1	Yes
7	propane	20.00	170	1.510	1.030	-	No
8	R32	20.00	170	1.410	0.923	27.1	No
9	R32	20.00	170	1.710	1.120	26.4	Yes

The pressure changes under the No. 4 and No. 9 conditions are shown in Figs 11 and 12, respectively. As the molybdenum wire was fused within 5 ms after the electricity application, the pressure began to increase: under No. 4 conditions, it started to rise rapidly from around 200 ms after the energy input and reached maximum of approximately 7.3 MPa after 300 ms (Fig. 11); in the condition No. 9, the pressure raised rapidly also from around 200 ms but it peaked at 400 ms reaching maximum of approximately 10.5 MPa.

The propagation of the disproportionation reaction is shown in Fig. 13 (crosses indicate that the reaction propagated, while circles indicate that the reaction did not propagate). By admixing propane or R32, the pressure limit of the disproportionation reaction shifted upward compared to pure HFO-1123, leading to suppression of disproportionation; however, the influence on the maximum pressure after reaction occurrence is small.

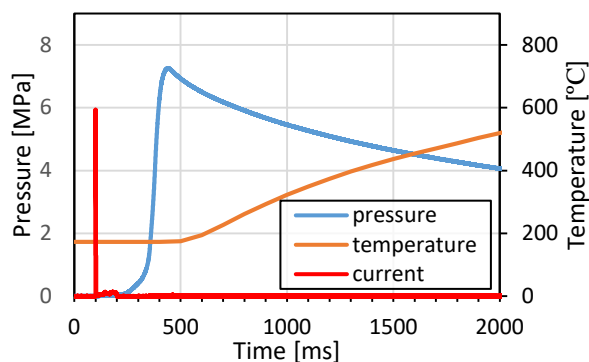


Fig. 11. Pressure and temperature change (No. 4).

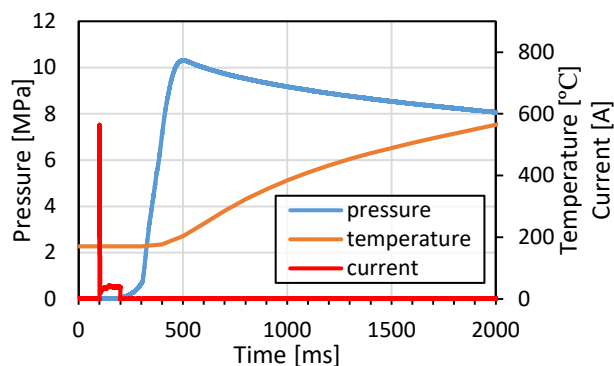


Fig. 12. Pressure and temperature change (No. 9).

5.2 Theoretical consideration of the reaction suppression

It was investigated whether the boundary of propagation of the disproportionation reaction can be predicted using the combustion model when R32 or propane are mixed with HFO-1123. The reaction order was set as $N = 4$, the pressure in Equation (6) was replaced with the partial pressure of HFO-1123 assuming that the R32 and propane were not involved in the reaction.

Fig. 13 shows the equivalent energy line for each mixed composition, and the experiment results. It was predicted that the pressure boundary of propagation of the disproportionation reaction would rise with increasing concentration of the mixture at constant energy input, mainly due to a decrease in the adiabatic flame temperature owing to increased heat capacity of the system. However, in the experiments, the boundary pressure increase was not proportional to the admixed concentrations and this point is not reflected in Equation (6). As observed in the experiment with 2.75-wt% propane mixture, the propagation pressure boundary was much higher than the linear interpolation between pure HFO-1123 and 20-wt% propane mixture; for R32, the propagation boundary pressure estimated by Equation (6) was much lower than the experimental one. The cause of this divergence is yet to be understood. The boundary of propagation of the disproportionation reaction depended greatly on the flame temperature, which accurate estimation should be a subject of future research.

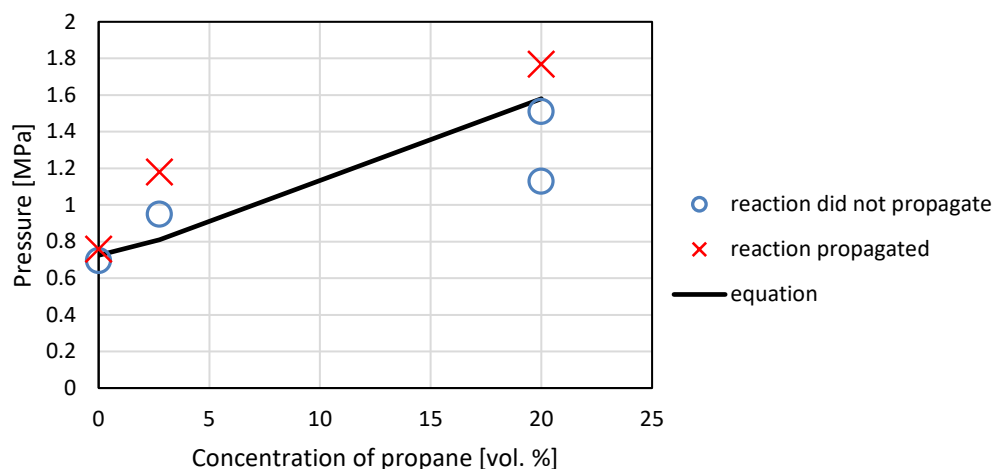


Fig. 13. Suppression of the disproportionation reaction by addition of propane.

6. CONCLUSIONS

Energy was applied under various temperature and pressure conditions, by melting a molybdenum wire, to pure HFO-1123 and its mixture with other substances in a metallic pressure vessel. Propagation of the HFO-1123 disproportionation was measured. Based on the obtained experimental results, the inhibiting effect on the reaction of mixing other substances into HFO-1123 was evaluated. It was found that the reaction can be suppressed by admixing propane or R32 refrigerant. To evaluate the inhibitory effects, a theoretical investigation of propagation of the disproportionation reaction is important.

NOMENCLATURE

B	constant	(dimensionless)
C_p	heat capacity at constant pressure	($\text{kJ kg}^{-1} \text{K}^{-1}$)
D	constant	(dimensionless)
d_{\min}	quenching distance	(m)
E	activation energy	(J)
E_{\min}	minimum ignition energy	(J)
N	reaction order	(dimensionless)

p	pressure	(Pa)
R	gas constant	(J mol ⁻¹ K ⁻¹)
S	burning velocity	(m s ⁻¹)
T	temperature	(K)
T _b	adiabatic flame temperature	(K)
λ	thermal conductivity	(W m ⁻¹ K ⁻¹)
ρ	density	(mol m ⁻³)
ω	reaction rate	(kg m ⁻³ s ⁻¹)

Subscript

u properties of the unreacted gas around the flame sphere

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