Electrical Breakdown Characteristics of Supercritical Trifluoroiodomethane-Carbon Dioxide (CF_3I-CO_2) Mixtures

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***Abstract*- Supercritical fluids (SCFs), as a new type of dielectric medium, combine highly desirable properties of gaseous and liquid dielectrics, most notably: low viscosity, high heat transfer capability, and high dielectric strength. This paper, for the first time, reports the results of breakdown experiments on the mixture of trifluoroiodomethane (CF_3I) and carbon dioxide (CO_2) under the supercritical conditions. Experiments were conducted in a 0.1 mm gap under a uniform electric field. The state of substance during experiments was obtained by the calculation from the equation of state (EoS), and by evaluating the optical appearance. The experiment result shows a dielectric strength of the supercritical CF_3I-CO_2 mixture at an average of 278 kV/mm with a 10% CF_3I mass fraction. Our experiments also suggest that the dielectric behavior of this supercritical CF_3I-CO_2 mixture manifests a discontinuity of the dielectric strength near the critical point. This paper indicates the suitability of using supercritical CF_3I-CO_2 mixture for high power density applications.**

I. Introduction

Supercritical fluids (SCFs), a state achieved when temperature and pressure are above the critical point, as shown in Fig. 1, have been widely studied and applied in the field of chemistry, including polymer processing, drying, and extraction of products from natural materials [1]. Recently, SCFs have drawn attention in the area of electrical discharge: not only for chemical synthesis and nanomaterials fabrication [2] but also on utilizing SCFs as dielectric media for power applications [3, 4]. Specifically, Zhang *et al.* demonstrated a supercritical nitrogen (N_2) plasma switch and showed that supercritical N_2 exhibits excellent dielectric properties and recovery behavior from breakdown [5, 6]. Kiyan *et al.* conducted research on the pre-breakdown and breakdown in supercritical carbon dioxide (CO_2) with different electrode geometries and revealed a polarity effect in supercritical CO_2 [7, 8]. Besides investigations on pure substances such as supercritical N_2 and supercritical CO_2, our previous study has focused on the breakdown characteristics of supercritical carbon dioxide-ethane (CO_2-C_2H_6) mixtures. The study found that mixtures of SCFs can yield a useful combination of properties such as the dielectric strength and the critical point, thus allowing for a broader range of applications [9]. A theoretical model was developed to describe the mechanism of electrical breakdown in supercritical CO_2 with molecular clusters formation. By analyzing the cross-section data of clusters, it has been confirmed that the cross-section data of clusters decrease from those of gases [10-12].

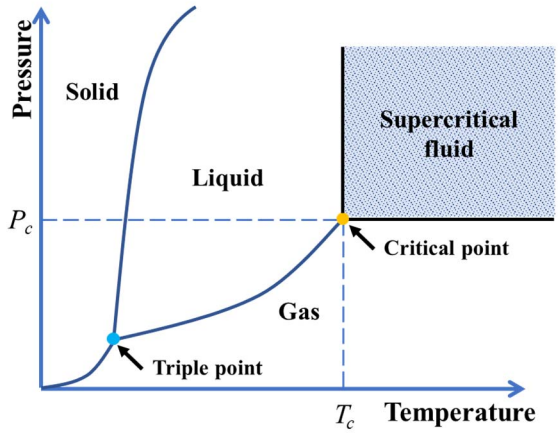

Fig. 1 A typical phase diagram. It shows four distinct thermodynamic phases, including solid, liquid, gaseous, and supercritical fluid.

Trifluoroiodomethane (CF_3I), as one of the candidates of sulfur hexafluoride (SF_6) alternatives, has several beneficial physical properties. It is nonflammable, colorless, and chemically stable. In addition, CF_3I has a low global warming potential (GWP) of 0.4 against approximately 22,800 for SF_6. Also, the overall atmospheric lifetime of CF_3I is very short due to the weak chemical bond C-I. A comparison of some important physical properties is given in Table 1 [13-15].

Table 1. Physical properties of SF_6, CO_2, and CF_3I.

	Molecular formula	T_c (K)	P_c (MPa)	GWP	Atmospheric lifetime (Years)
Carbon dioxide	CO_2	304.2	7.39	1	200
Trifluoroiodomethane	CF_3I	395.2	4.04	0.4	30 (days)
Sulfur Hexafluoride	SF_6	318.7	3.76	22,800	3,200

Although extensive research has been carried out on the electric discharge generated in supercritical CO_2 and N_2, there is no consideration of many other highly promising supercritical substances or mixtures. Especially, for power applications, there has not been any investigation of the SF_6

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alternatives in the supercritical state. Similarly, although numerous research efforts have focused on the insulation performance of CF_3I and its mixtures with CO_2 and N_2 over the past few years [16-18], these studies were all conducted in the gaseous phase, which suffers under limited heat transfer and dielectric strength compared to SCFs. In this paper, we demonstrate, to the best of our knowledge, the first experimental measurement on the breakdown characteristics of a supercritical CF_3I-CO_2 mixture.

II. Experimental Setup

A. Breakdown test setup

A complete setup with the high pressure chamber (A), a temperature-controlled water bath (B), pressure gauges (C), a thermal control system (D and E), a high precision scale, and control valves, is assembled and built as shown in Fig. 2. The electrode on the high voltage side is attached to the brass conductor, and the grounded electrode is clamped by a stainless steel plate that is supported and electrically grounded by three stainless steel rods (F). The copper electrodes (G) have a spherical geometry with a diameter of 20 mm.

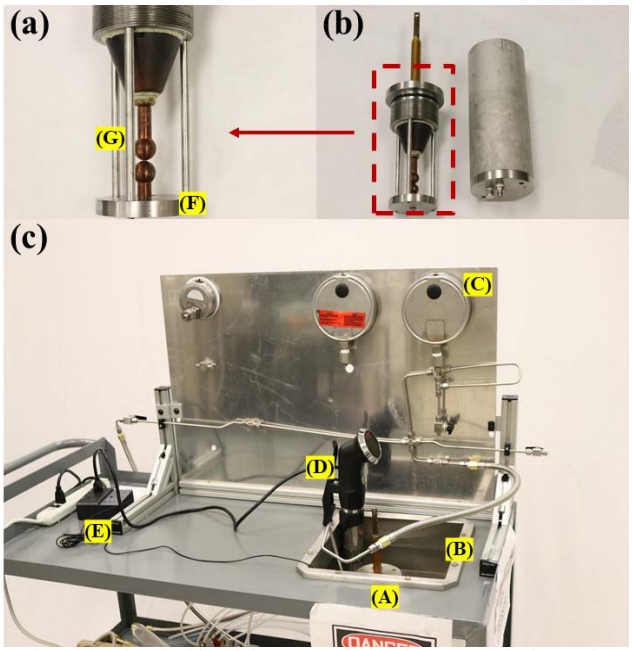

Fig. 2 The electrical breakdown experimental setup. (a) the internal configuration of the chamber, (b) the external view of the high pressure bushing and the body of the high pressure chamber, (c) the testbed for the SCF breakdown experiment, which contains a temperature-controlled bath, pressure gauges, and a thermal control system.

The experiments were conducted under DC voltage (Spellman SL60PN1200, rated 60 kV and 20 mA). The voltage was ramped up at 0.5 kV/s, and the gap between the two electrodes was set to be 0.1 mm. The gap is measured by a stainless steel feeler gauge with accuracy within ±5%. The breakdown voltage was then measured and recorded fifteen times at each condition. The accuracy of the voltage measurement is estimated to be within ±3%. The average breakdown voltage and the corresponding scattering data were calculated based on these fifteen measurements. The time interval between two successive breakdown events was about two minutes to reduce the effect of the medium state variation caused by the arc discharge and allow discharge products to move away from the zone of the highest electric field.

B. Experimental conditions and isothermal properties

Sometimes, SCF can be represented as an intermediate state between gas and liquid states; it combines the properties of both phases such as low viscosity like a gas, and effective heat transfer capabilities like a liquid. In addition to these physical properties, which are promising for a wide range of applications, SCFs also offer high dielectric strength due to its high density. Therefore, more research projects have been conducted in utilizing SCFs as dielectric and insulating media in power applications.

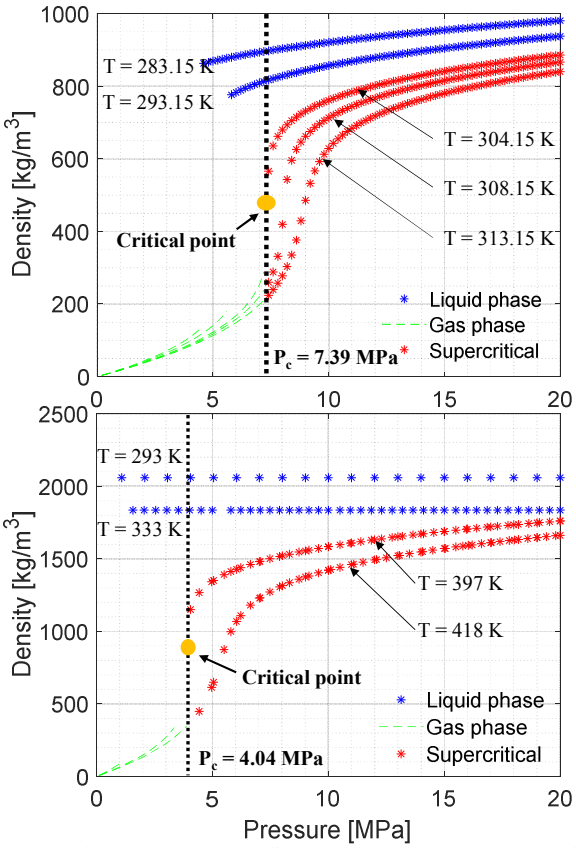

Fig 3. Density – pressure (ρ - P) diagrams of CO_2 (above) and CF_3I (below) with isothermal lines. The critical points for each substance are represented by the yellow dot at T_c = 304.2 K, P_c = 7.39 MPa (CO_2) and T_c = 395.2 K, P_c = 4.04 MPa (CF_3I) [19-21].

Fig. 3 shows density – pressure (ρ–P) diagrams of both CO_2 (above) and CF_3I (below) with isothermal lines. Green dashed lines represent the fluid in the gaseous phase. Blue and red asterisks represent the fluid in the liquid phase and the supercritical state, respectively. The critical points are represented by the yellow dots. Near the critical point, small changes in the medium pressure result in significant changes in the density. Critical anomalies can be observed in the

vicinity of the critical point, such as maximum values of thermal conductivity and heat capacity.

The critical point of the CF_3I-CO_2 mixture at 10% CF_3I mass fraction is acquired from the equation of state (EoS) [19, 20]. Specifically, the calculation of the critical point (T_c, P_c) of a supercritical mixture is based on solving equations including the mathematical definition of critical point [22] and the EoS of corresponding substances:

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \quad (1)$$

and two determinants of multicomponent mixture provided by Gibbs [23]:

$$D_1 = det\left|\frac{\partial^2 G}{\partial x_i \partial x_j}\right| = 0 \quad (2)$$

$$D_2 = det\left|(1-\delta_{ki})\frac{\partial^2 G}{\partial x_i \partial x_j} + \delta_{ki}\frac{\partial D_1}{\partial x_j}\right| = 0 \quad (3)$$

where V is the volume, P is the pressure, Tc represents the critical temperature, G is Gibbs energy, x_i is composition of component i, k is a constant.

The calculated critical point of this mixture (T_c = 315.0 K, P_c = 7.20 MPa) is in good agreement with the optically determined critical point using a high pressure optical vessel.

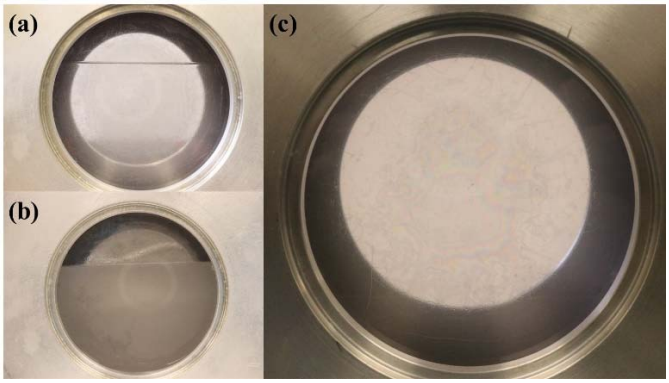

Fig 4. Determination of the critical point of a sample of CF_3I-CO_2 at 10% CF_3I mass fraction by observing the critical opalescence. (a) the medium at a temperature below its critical point ($T < T_c$), (b) the medium at a temperature near its critical point ($T \approx T_c$), (c) the medium at a temperature above its critical point ($T > T_c$).

III. Results & Discussions

To identify the state of the CF_3I-CO_2 mixture inside the high pressure chamber, the critical point needs to be determined. Besides the critical values calculated by the EoS, a static equilibrium apparatus, as shown in Fig. 4, was also built to replicate the experimental condition and to confirm the critical points visually. Specifically, the critical opalescence is observed to determine the critical state of such a binary mixture. Fig. 4 shows a sample of this mixture with gravity directed downward. In Fig. 4(a) the temperature is below its critical point: two distinct phases exist. The boundary between gas and liquid is visible. As the temperature rises, the gas-liquid phase boundary starts to vanish, as shown in Fig. 4(b). Fig. 4(c) shows the sample significantly above its critical point, the phase boundary disappears. As a result, the critical point observed from the optical chamber is T_c = 317.5 K, P_c = 7.25 MPa, which is in good agreement with the critical point calculated from the EoS (T_c = 315.0 K, P_c = 7.20 MPa).

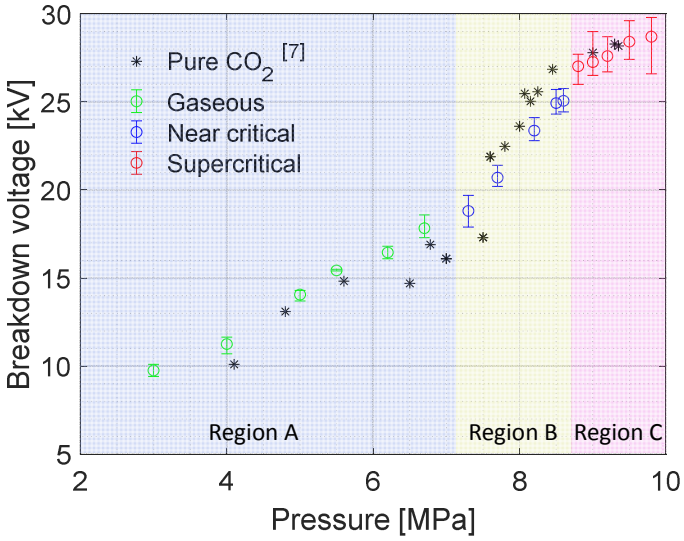

Fig 5. Experimental results for the breakdown voltage of supercritical CF_3I-CO_2 mixture up to 10 MPa in a uniform electric field at a 0.1 mm gap at a temperature of 323 K. The mass fraction of CF_3I is 10%. The black asterisks indicate the average of the measurement data of pure CO_2 [9]. Open circles represent the average breakdown voltage, and vertical error bars represent the corresponding experimental scattering data.

The breakdown voltage measurements were carried out at a temperature of 323 K (50°C) from the gaseous phase to the supercritical condition. Fig. 5 shows the measured breakdown voltages as a function of the pressure. The average breakdown voltage of fifteen measurements and their scattering data at one experimental condition are represented by an open circle and a vertical error bar. The result also shows a comparison of the dielectric strength measurement of this CF_3I-CO_2 mixture with experimental results of pure CO_2 [9]. The result indicates that the breakdown strength of the CF_3I-CO_2 mixture in the gaseous phase is, in general, higher than those of pure CO_2, even for only a 10% CF_3I mass fraction (region A). At the situation near the critical point, the CF_3I-CO_2 mixture exhibits a discontinuity of the slope where the substance undergoes a phase change (region B). Such a discontinuity can be explained from the microscopic point of view by the molecular clustering, as well as the macroscopic point of view by the density fluctuation. It can also be estimated that the density fluctuation of this binary mixture reaches a maximum near 8.8 MPa, which also represents a boundary surface that separates the supercritical region into gas-like phases and liquid-like phases. In the supercritical state, the breakdown voltage of both CF_3I-CO_2 mixture and pure CO_2 have a trend to saturate at higher densities (region C). However, no

significant difference is observed on the dielectric strength of the pure CO_2 and CF_3I-CO_2 (10% mass fraction of CF_3I) mixture at the supercritical state. This is not very surprising since a 10% of CF_3I mass fraction in this binary mixture fluid is only equivalent to a 2.4% of mole fraction. Although it is easier to use the mass fraction for experiments, the mole fraction is a better measure to understand the impact onto the dielectric strength from an electronic point of view since it correlates with the probability of electron-molecule collisions with one over the other constituents. In this case, a 2.4% mole fraction of CF_3I indicates that electrons only rarely collide with the strongly electronegative CF_3I molecules, i.e. the overall effect onto the dielectric strength is limited.

IV. Conclusions

In this study, we conducted breakdown measurements of supercritical CF_3I-CO_2 mixture with a CF_3I mass fraction of 10% at 323 K. We also compared the result with our previous breakdown strength measurement of pure supercritical CO_2. Experimental conditions such as electrode geometry and gap distance were maintained, except for the experimental temperature (two dielectric fluids have different critical temperatures). Moreover, we showed the breakdown strength of CF_3I-CO_2 at the supercritical state, which is higher than that in the gaseous phase. Meanwhile, since the critical temperature of the CF_3I-CO_2 mixture at 10% CF_3I mass fraction is only about 10 K above the critical temperature of pure CO_2, no additional temperature withstanding capability is necessary to implement this new dielectric medium. Experimental investigations on the dielectric strength of this mixture at higher CF_3I mass fraction will be conducted in the near future. This study also indicates the suitability of using SCF mixtures as dielectric and insulating media for applications that require efficient heat dissipation, high-speed motion, and strong electric fields.

Acknowledgment

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References

[1] C. A. Eckert, B. L. Knutson, and P. G. Debenedetti, "Supercritical fluids as solvents for chemical and materials processing," *Nature,* vol. 383, no. 6598, p. 313, 1996.

[2] S. Stauss, H. Muneoka, K. Urabe, and K. Terashima, "Review of electric discharge microplasmas generated in highly fluctuating fluids: characteristics and application to nanomaterials synthesis," *Physics of Plasmas,* vol. 22, no. 5, p. 057103, 2015.

[3] J. Wei, A. Cruz, C. Xu, F. Haque, C. Park, and L. Graber, "A Review on Dielectric Properties of Supercritical Fluids," in *2020 IEEE Electrical Insulation Conference (EIC)*, 2020: IEEE, pp. 107-113.

[4] C. Xu, J. Wei, and L. Graber, "Compatibility Analysis of Piezoelectric Actuators in Supercritical Carbon Dioxide," in *2020 IEEE Electrical Insulation Conference (EIC)*, 2020: IEEE, pp. 171-174.

[5] J. Zhang *et al.*, "Breakdown strength and dielectric recovery in a high pressure supercritical nitrogen switch," *IEEE Transactions on Dielectrics and Electrical Insulation,* vol. 22, no. 4, pp. 1823-1832, 2015.

[6] J. Zhang, B. van Heesch, F. Beckers, T. Huiskamp, and G. Pemen, "Breakdown voltage and recovery rate estimation of a supercritical nitrogen plasma switch," *IEEE Transactions on Plasma Science,* vol. 42, no. 2, pp. 376-383, 2014.

[7] T. Kiyan *et al.*, "Negative DC prebreakdown phenomena and breakdown-voltage characteristics of pressurized carbon dioxide up to supercritical conditions," *IEEE transactions on plasma science,* vol. 35, no. 3, pp. 656-662, 2007.

[8] T. Kiyan *et al.*, "Polarity effect in DC breakdown voltage characteristics of pressurized carbon dioxide up to supercritical conditions," *IEEE transactions on plasma science,* vol. 36, no. 3, pp. 821-827, 2008.

[9] J. Wei, C. Park, and L. Graber, "Breakdown characteristics of carbon dioxide–ethane azeotropic mixtures near the critical point," *Physics of Fluids,* vol. 32, no. 5, p. 053305, 2020, doi: 10.1063/5.0004030.

[10] Y. Tian, J. Wei, C. Park, Z. Wang, and L. Graber, "Modelling of electrical breakdown in supercritical CO 2 with molecular clusters formation," in *2018 12th International Conference on the Properties and Applications of Dielectric Materials (ICPADM)*, 2018: IEEE, pp. 992-995.

[11] F. Haque, J. Wei, L. Graber, and C. Park, "Modeling the dielectric strength variation of supercritical fluids driven by cluster formation near critical point," *Physics of Fluids,* vol. 32, no. 7, p. 077101, 2020, doi: 10.1063/5.0008848.

[12] F. Haque, J. Wei, L. Graber, and C. Park, "Electron Scattering Cross Section Data of Supercritical CO 2 Clusters," in *2020 IEEE Electrical Insulation Conference (EIC)*, 2020: IEEE, pp. 144-147.

[13] L. Graber, "Improving the accuracy of SF 6 leakage detection for high voltage switchgear," *IEEE Transactions on Dielectrics and Electrical Insulation,* vol. 18, no. 6, pp. 1835-1846, 2011.

[14] J. De Urquijo, "Is CF3I a good gaseous dielectric? A comparative swarm study of CF3I and SF6," in *Journal of Physics: Conference Series*, 2007, vol. 86, no. 1: IOP Publishing, p. 012008.

[15] P. Forster *et al.*, "Changes in atmospheric constituents and in radiative forcing. Chapter 2," in *Climate Change 2007. The Physical Science Basis*, 2007.

[16] X. Zhao, B. Li, D. Xiao, and Y. Deng, "Breakdown characteristics of CF3I-N2 gas mixtures in a needle-plate geometry," *IEEE Transactions on Dielectrics and Electrical Insulation,* vol. 24, no. 2, pp. 869-875, 2017.

[17] L. Chen, H. Griffiths, A. Haddad, and M. Kamarudin, "Breakdown of cf 3 i gas and its mixtures under lightning impulse in coaxial-GIL geometry," *IEEE Transactions on Dielectrics and Electrical Insulation,* vol. 23, no. 4, pp. 1959-1967, 2016.

[18] H. Katagiri, H. Kasuya, H. Mizoguchi, and S. Yanabu, "Investigation of the Performance of CF 3 I Gas as a Possible Substitute for SF 6," *IEEE Transactions on Dielectrics and Electrical Insulation,* vol. 15, no. 5, pp. 1424-1429, 2008.

[19] H. W. Xiang, "Vapor pressures, critical parameters, boiling points, and triple points of halomethane molecular substances," *Journal of Physical and Chemical Reference Data,* vol. 30, no. 5, pp. 1161-1197, 2001.

[20] S. A. Kudchadker and A. P. Kudchadker, "Ideal gas thermodynamic properties of CH4−(a+ b+ c+ d) F a Cl b Br c I d Halomethanes," *Journal of Physical and Chemical Reference Data,* vol. 7, no. 4, pp. 1285-1308, 1978.

[21] E. Lemmon, M. McLinden, D. Friend, P. Linstrom, and W. Mallard, "NIST chemistry WebBook, Nist standard reference database number 69," *National Institute of Standards and Technology, Gaithersburg,* 2011.

[22] P. A. Rock, *Chemical thermodynamics*. University Science Books, 1983.

[23] J. Gibbs, "The Scientific Papers of J. Willard Gibbs:"On the Equilibrium of Heterogeneous Substances", Vol. 1, Thermodynamics," ed: Ox Bow Press, Connecticut, 1876.