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Experimental studies on the flammability of mixtures of dimethyl ether

Qi Chen [a,b], JiWei Yan [a,b], Guangming Chen [a,b,*], Yang Zhao [c], Yuqi Shi [a,b], Zhaoyun Zeng [a,b], Qinglei Pan [a,b]

[a] Institute of Refrigeration and Cryogenics, Zhejiang University, Hangzhou, 310027, China
[b] State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou, 310027, China
[c] Zhejiang Quhua Fluorine Chemistry Co., Ltd., China

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A B S T R A C T

According to the standard of American Society for Testing Materials, an experimental apparatus for testing flammability of flammable refrigerants was developed. Its reliability was validated subsequently. Studies on dimethyl ether have been performed since it's considered as one of the most alternative substitute for R134a. No experimental or theoretical study has been conducted on the flammability of the binary mixture DME/R134a so far. In this paper, the flammability data of the binary mixture DME/R134a with different volume ratios were tested, the corresponding explosion limits and critical flammability ratio were also obtained. The results show that when the volume ratio of the flame retardant R134a to the flammable refrigerant DME is about 5, the binary mixture reaches its critical flammability ratio. R1234yf is a new and promising alternative, its ternary mixture DME/R1234yf/R134a shows promise as a new air-conditioning refrigerant, a explosion limit was tested and the critical suppressive line of the ternary mixture DME/R1234yf/R134a was presented. The flammability data is of great importance in manufacture and application of the new flammable refrigerants.

1. Introduction

Because of the Montreal Protocol on Substances that Deplete the Ozone Layer, R12 and other traditional refrigerants are regulated in ozone depleting. Substituting for CFCs, R134a has been the main product on the market since its many merits: good thermal performance, zero ozone depleting potential (ODP), nontoxic and nonflammable. However, its global warming potential (GWP) is as high as 1370 which does not meet the requirement of the Kyoto Protocol. Therefore, it is urgent to develop new refrigerants with better environmental performance and congruous thermal performance with R134a. Over the years, some alternative refrigerants such as R407C and R407A have been developed, but their chemical and/or physical performance is unsatisfactory and values of GWP are high.

Dimethyl ether (DME) belongs to oxygenated compounds, and has being widely utilized in chemical industry, medicine and other fields due to its outstanding advantages. DME is regarded as an alternative refrigerant with low boiling point, large latent heat, non-toxic, poor corrosion and other properties. Compared with conventional halogenated hydrocarbons R12, R22 and R134a, DME is more environmental friendly since its ODP and GWP are 0, and its market price is only about one-half, one-third and one-seventh of those of R12, R22 and R134a, respectively. Research results have indicated that cooling effect of DME and its mixtures is similar to that of R134a. There is a potential for DME to replace R134a.

Recently, a number of literatures have reported on the properties of DME [1–6]. But studies regarding its flammability characteristics are comparatively few [7–9]. And for all we know, studies on the flammability of mixtures DME/R134a and DME/R1234yf/R134a have not been presented. More experimental and theoretical works are indispensible to provide better understanding for the real industrial application.

Based on the above research, experimental studies on the flammability of the mixed refrigerant DME/R134a and DME/R1234yf/R134a have been performed in this paper. Furthermore, the critical suppressive line of DME/R1234yf/R134a is presented theoretically.

2. Experimental apparatus

For materials with large quenching distances which may be difficult to ignite, a method (ASTM E681-09) for determination of

* Corresponding author at: Institute of Refrigeration and Cryogenics, Zhejiang University, 38 Zheda Road Hangzhou, 310027, China. Tel.: +86 87951680.
E-mail address: gmchen@zju.edu.cn (G. Chen).

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explosion limits has been proposed by American Society for Testing Materials [10]. According to this standard, an experimental apparatus for flammability tests has been developed by Zhejiang University, as shown in Fig. 1.

Being divided into gas-distribution side and experimental side, the apparatus employs a spherical pressure-resistant flask with a volume of 12 L. Two ignition electrodes are put symmetrically at its center and one third the diameter of the flask from the bottom of the flask. For spark discharge ignition, the two discharge electrodes are positioned with a 6 mm gap between them, and a direct current is discharged with a maximum voltage of 15 kV for an interval of 0.4 s. As a safety precaution, the glass flask is put into an iron box, which is equipped with a safety viewing window to observe experiment phenomenon.

For the flammability test, the humidity and temperature are very important. These two factors are controlled strictly according to the standard ASTM E681-09. The humidity is measured by PC-523-XX-T1 Temperature and Humidity Sensor with a full scale of 0–100% relative humidity. The temperature is measured by PT100 Platinum resistance with an error of $\pm 0.3\,^{\circ}C$. The pressure is measured using pressure transducer with an accuracy of 0.2% of full scale. The output signals from the measurement devices are transferred to a PC through the Agilent 34970A.

The experimental conditions are as following

Humidity: $\leq$5% relative humidity

Temperature: $21 \pm 1\,^{\circ}C$

Pressure: 0.1 MPa

The ratio error of each two substances is controlled not more than 0.21% during charging the gases. The concentration of the each flammable gas is measured with an accuracy of 0.4% or less.

3. Experimental principle and process

3.1. Experimental principle

As for the mixture DME/134a, both pure refrigerants and air are assumed to be ideal gas, which implies that the volume ratio of the flammable refrigerant DME in this study is equal to its partial pressure ratio in the mixture DME/R134a/air. The volume ratio of DME can be described as:

$$V = P_1/P \times 100\% \qquad (1)$$

where, V and P_1 are volume ratio and partial pressure of DME; P is total pressure of the mixture.

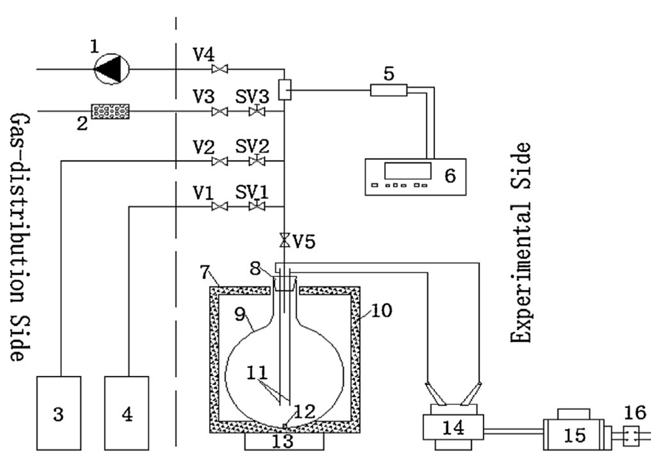

Fig. 1. Schematic of experimental apparatus for flammability tests. 1-vacuum pump; 2-dry filter; 3, 4-refrigerant tanks; 5-pressure transducer; 6-Agilent 34970A; 7-iron box; 8-rubber stopper; 9-spherical glass flask; 10-foam; 11-electrodes; 12-stirring bar; 13-magnetic stirrer; 14-potential transformer; 15-autotransformer; 16-time relay; V1 ~ V5-two-way valves; SV1 ~ SV3-solenoid valves.

3.2. Experimental process

3.2.1. Check the tightness of experimental apparatus

The tightness of the experimental apparatus should be examined. First, the spherical glass flask and the gas pipelines are evacuated to a pressure of 1.33 kPa or less. Then turn off the vacuum pump and ensure that the pressure increase rate of the flask must not be greater than 0.1 kPa/min.

3.2.2. Experimental procedure

(1) According to the theoretical prediction method [11], the explosion limits of flammable refrigerants are calculated.
(2) Evacuate the spherical flask and pipelines, introduce the refrigerants and dry air into the glass flask to a given pressure, respectively.
(3) Turn on the stirrer and continue stirring for at least 5 min until the mixture is homogeneous.
(4) Turn off the stirrer and record the parameters such as temperature, pressure, the relative humidity of the mixture and the ambient pressure.
(5) Two minutes later, activate the ignition source.
(6) Observe the flame phenomenon in the glass flask. According to the standard ASTM E681-09 [10], the criterion used to judge a mixture is explosive is that flames that having spread upward and outward to the walls of the flask, are continuous along an arc that is greater than 90°. For convenience of observation, a camera is employed to record and playback the phenomenon.
(7) Evacuate the system and introduce dry air to ensure removal of residual volatile materials for the next test.

To check the reliability of the experimental apparatus, the upper explosion limit and the lower explosion limit of R32 have been validated. As stated in the standard ASTM E681-09 [10], reproducibility for difficult-to-ignite materials between tests is 0.9 vol% for the lower explosion limit and 1.8 vol% for the upper explosion limit. The results in Table 1 prove that the reproducibility of the apparatus is excellent and it can satisfy the requirement of experiment consequently.

4. Results and discussion

Fig. 2 presents the variations in the concentration of the binary mixture R134a/DME with the volume ratio of the flame retardant R134a to the flammable refrigerant DME. In the figure, the solid line with triangle stands for the upper explosion limit of the binary mixture DME/R134a while the other with square stands for the lower explosion limit. The closed interval constituted by these two lines is the flammable zone, which indicates that the binary mixture will flame if its concentration and volume ratio fall into this zone simultaneously. The figure also shows that the upper explosion limit will be equal to the lower explosion limit when the volume ratio of R134a to DME is about 5. Besides, the lower explosion limit of the binary mixture increases obviously as R134a

Table 1
Comparison between experimental results and literature data of R32 ($21 \pm 1\,^{\circ}C$, 0.1 MPa).

	Experimental value				Literature value [12]	Absolute error
	Test1	Test2	Test3	Mean		
Lower limit (%)	13.99	14.01	13.98	13.99	14.4	−0.41
Upper limit (%)	31.98	32.01	31.96	31.98	31.0	+0.98