Minimum ignition energies and laminar burning velocities of ammonia, HFO-1234yf, HFC-32 and their mixtures with carbon dioxide, HFC-125 and HFC-134a

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Abstract

Given the safety issues associated with flammability characteristics of alternative environmentally-friendly refrigerants, it is vital to establish measurement systems to accurately analyse the flammability of these mildly flammable refrigerants. In this study, we used a customised Hartmann bomb analogue to measure the minimum ignition energy (MIE) and laminar burning velocity (BV) for refrigerant/air mixtures of pure ammonia (R717), R32, R1234yf and mixtures of R32 and R1234yf with non-flammable refrigerants of R134a, R125 and carbon dioxide (R744). The MIEs of R717, R32, and R1234yf were measured at an ambient temperature of 24 °C to be (18.0 ± 1.4), (8.0 ± 1.5) and (510 ± 130) mJ at equivalence ratios of 0.9, 1.27 and 1.33, respectively. Adding the non-flammable refrigerants R134a, R125 and R744 along with R32 at volumetric concentrations of 5% each to R1234yf reduced the latter compound’s flammability and increased its MIE by one order of magnitude. The laminar burning velocities of pure R717 and R32 were measured at an equivalence ratio of 1.1 using the flat flame method and found to be 8.4 and 7.4 cm/s, respectively. Adding 5% R1234yf to R32 decreased the laminar burning velocity by 11%, while a further 5% addition of R1234yf resulted in a decrease of over 30% in the laminar burning velocity.

Keywords: *Flammability Characteristics; Minimum Ignition Energy; Burning Velocity; Refrigerants; Hydrofluoroolefins; Hydrofluorocarbons;*

Nomenclature

BV	Laminar burning velocity	d_q	Quenching distance (mm)
CFC	Chlorofluorocarbon	E	Energy (mJ)
GWP	Global warming potential	F	Farad
HFC	Hydrofluorocarbon	φ	Equivalence ratio
HFO	Hydrofluoroolefin	H	Henry
ID	Interior diameter	i, I	Current (amp)
MIE	Minimum ignition energy	P	Power (mJ/s)
mol	Fraction by mole	R	Resistance (Ohm)
OD	Outside diameter	Ω	Ohm
ODP	Ozone depletion potential	ρ	Density (kg/m^3)
vol	Fraction by volume	T	Temperature (K)
wt	Fraction by weight	v, V	Voltage (Volt)
Symbols		δ	Flame thickness (mm)
c_p	Specific heat at constant pressure (J/kg.K)		
d_{min}	Minimum quenching distance (mm)		

1. Introduction

Following the adoption of the Kyoto Protocol [1] and changes in the regulations of many countries to control the emissions of high global warming potential (GWP) refrigerants [2], substantial research has begun to replace the current high-GWP working fluids of the cooling systems with alternative refrigerants [3]. Hydrofluoroolefins (HFOs) are the latest generation of environmentally friendly refrigerants that can only survive in the atmosphere for merely a few days because of the weak double bonds in their structure. As a result, the GWP for HFOs is considerably lower (less than 1) than hydrofluorocarbons (HFCs); in contrast, HFC-134a is one of the most popular refrigerants with a GWP of ~1430. However, the performance of HFOs in current refrigerators is inferior, as they consume larger amounts of energy to deliver a similar cooling power [4]. Besides, mild flammability of HFOs poses a risk for their domestic applications, such as air conditioning systems, potentially causing fire or emitting hazardous combustion products. Blending HFOs with non-flammable refrigerants – including HFCs and natural refrigerants – could boost their performance, decrease the mixtures' GWP, and minimise their flammability [5]. For example, R1234yf and R32 are two compounds compatible with conventional refrigeration systems, including new automobile air conditioners, that can be used to make low GWP refrigerant blends with a reasonable cooling performance [6].

The ASHRAE standard 34, "Designation and Safety Classification of Refrigerants" [7], categorises R32 and R1234yf as mildly flammable substances. Table 1 presents this classification in terms of safety and toxicity, where R32 and R1234yf fall into the A2L classification. Risks associated with these refrigerants include a high contribution to the accumulation of trifluoroacetic acid (TFA) in the atmosphere [6] and toxic combustion products such as hydrogen fluoride (HF) and carbonyl fluoride (COF_2) [8,9]. Therefore, the flammability characteristics of these refrigerants and their mixtures with non-flammable candidates must be addressed carefully and accurately.

Table 1: Safety classifications of refrigerants: (A) and (B) represent refrigerants with lower and higher toxicity, respectively [7].

	Safety Group	
Higher Flammability	A3	B3
Lower Flammability	A2	B2
	A2L*	B2L*
No Flammability	A1	B1
Toxicity	Lower	Higher

* A2L and B2L refrigerants have burning velocities lower than 10 cm/s.

The flammability characteristics of pure R32 and R1234yf in mixtures with air including their lower flammability limit (LFL), minimum ignition energy (MIE) and maximum laminar burning velocity (BV) have been investigated and reported in the literature [10–15]. Nevertheless, the reported results suffer from a paucity of consistency – caused by a wide variety of measurement approaches and procedures – that makes fire risk assessment demanding and potentially unreliable. Table 2 presents the different MIE values reported for refrigerant/air mixtures containing R32, R1234yf and R717. The reported MIE values of R32 in the literature range from 14 mJ [14] to 26,300 mJ [16]. Similarly, the reported MIE of R1234yf varies from (less than) 500 mJ [17] to 10,000 mJ [18]. The MIE of R717 was reported between 8 mJ [19] and 300 mJ [18]. Spark specifications were reported to be the main source of the variation in the MIE values [20]. Thus, the measured MIE values for a given refrigerant obtained with a specific measurement system can at least be compared with the values obtained for other compounds using the same apparatus under similar conditions.

Table 2: Reported minimum ignition energies for R717, R32, and R1234yf.

Compound	Ignition Method	Equivalence Ratio[*]	MIE/mJ	Ref.
R717	Spark Energy (Capacitive)	0.90	8	[19]
	Estimated	1.00	19	[14]
	Estimated	1.00	20	[18]
	Spark Energy (Capacitive)	1.00	50-100	[21]
	Spark Energy (Capacitive)	Not given	170	[21]
	Spark Energy (Capacitive)	1.00	100-300	[18]
R1234yf	Spark Energy (Capacitive)	1.32	<500	[9]
	Estimated	1.33	780	[14]
	Spark Energy	1.00	1500	[9]
	Estimated	1.00	2000	[18]
	Spark Energy (Capacitive)	Not given	5000-10000	[18]
R32	Estimated	1.27	14	[14]
	Estimated	1.27	20	[14]
	Estimated	1.00	20	[18]
	Spark Energy (Capacitive)	Not given	30-100	[18]

Bunsen burner, spherical vessel, and particularly vertical tube are the main laminar burning velocity measurement systems reported in the literature [13,22,23]. Jabour et al. [12,24] used a vertical tube to measure the BV of a series of refrigerants such as R32 and R717. They measured the BV at stoichiometric concentrations to be 6.5 cm/s and 7 cm/s for R32 and R717, respectively. Takizawa et al. [11] also measured the BV of R32 by the vertical tube method and found a maximum value of 6.2 cm/s for an R32 + air mixture at 19.2 vol%. Fuller et al. [23] proposed a new approach, known as the flat flame method, which enables a more direct measurement of the BV. In this arrangement, the effect of buoyancy on the flame was eliminated, and a one-dimensional flat flame was formed after ignition, which propagates downward at the mixture's BV. They used this method to measure the BV of propane + air mixture at 4 mol% to be 40 cm/s. For the same mixture and using a similar method, Bockhorn et al. [25] reported the BV to be 37 cm/s.

In this study, the flammability of pure R32, R1234yf, R717 and mixtures of R32 and R1234yf with non-flammable refrigerants such as R125, and R134a and R774 (CO_2) was evaluated by measuring their MIE and Laminar BV. The MIE of the pure components of R32, R1234yf and R717 was measured using a customised Hartmann bomb analogue. To analyse the MIE of the refrigerants, the current and high voltage supplied to the discharge circuit to generate the spark were measured precisely during the ignition process. Furthermore, the effect of adding non-flammable refrigerants on the MIEs of R32 and R1234yf was investigated. Finally, the laminar BV of pure R717, R32 and mixtures of R32 and R1234yf was measured directly with the flat flame method, and the results compared with those in the literature.

2. Experimental

2.1 Minimum Ignition Energy

The details of the gases used in this work are presented in Table 3.

Table 3: Details of the pure refrigerants and air used in this study.

ASHRAE refrigerant number	IUPAC name	Chemical formula	CAS #	Supplier	Purity[a]
R32	Difluoromethane	CH_2F_2	75-10-5	Core gas	0.995
R125	Pentafluoroethane	C_2HF_5	354-33-6	Core gas	0.995
R134a	1,1,1,2-Tetrafluoroethane	$C_2H_2F_4$	811-97-2	Core gas	0.995
R1234yf	2,3,3,3-Tetrafluoropropene	$C_3H_2F_4$	754-12-1	Core gas	0.995
R744	Carbon Dioxide	CO_2	124-38-9	Core gas	0.99995
R717	Ammonia	NH_3	7664-41-7	BOC	0.9999
Air	Zero Grade Air	$O_2 + N_2$	132249-10-0	Core gas	0.21 ± 0.005 O_2

[a] Based on the supplier's specification (mole fraction).

The measurement of MIE for the selected refrigerants was conducted by the Hartmann bomb approach according to the British Standard EN 1839 [26]. We described the details of the original Hartman bomb setup in the supplementary information (SI). To safely discharge the toxic combustion products, we adapted the existing Hartmann bomb setup to use a cylindrical tube vessel. As shown in Figure 1, the new setup had a similar configuration to the Hartmann bomb, but the ignition vessel is connected directly to a neutralising system, which is described in detail in the SI. The ignition vessel consisted of a transparent vertical tube with 40 mm ID and 1500 mm length, closed at both ends with two caps. The lower end cap (ignition cap) was equipped with two tungsten electrodes (3.2 mm OD) providing the spark for ignition. It also included a gas inlet connection and an inline pressure transducer (DJ Instruments thro-FLU DF2). Both caps had quenching plates to prevent the flame from transferring into the gas lines. The commissioned MIE measurement system was validated by measuring pure R717 and R32 and comparing the results with the obtained values using our original Hartmann bomb apparatus.

A gas mixture preparation setup was applied to make mixtures of the refrigerants + air. The gas mixing setup consisted of several mass flow controllers (MFCs, Alicat Scientific MCS-1SLPM-D-IN-5M), where each MFC was connected to a pure gas cylinder. A small cylindrical container equipped with a stirrer was linked to the output of the MFCs to make the blends more homogenous. By setting the gas flow rates of the MFCs, it was possible to prepare a mixture with the desired composition. Before ignition, the prepared mixture flowed through the measurement system for 20 minutes, sufficient to purge the vessel's volume at least eight times. The temperature of the gas mixture was maintained constant at around 24 °C by using a heater inside the fume enclosure surrounding the ignition vessel and the gas mixing setup (Figure 1).

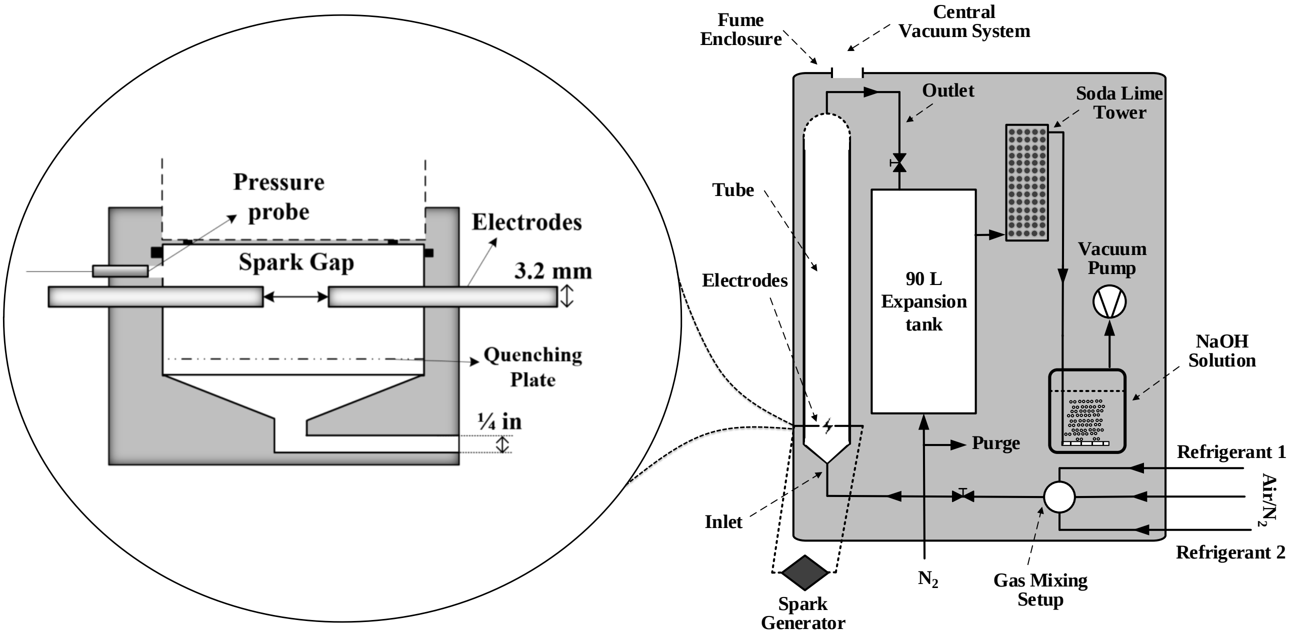


Figure 1: The schematic of the minimum ignition energy measurement system, including the effluent neutralisation and treatment components.

A high voltage spark generator – similar to that used by Lee and Shepherd et al. [27] – was connected to the electrodes in the measurement configuration to enable measurement of the minimum energy to ignite the flammable mixture. Further details are provided in the SI. The top-end cap of the ignition vessel was connected to a 90 L expansion tank to minimise the pressure rise in the vessel caused by the ignition. A vacuum pump (Varian SH-110) drew the toxic and corrosive products through the neutralisation system, which included a sodium hydroxide solution and a soda-lime tower.

2.2. Laminar Burning Velocity

The flat flame approach was used for the laminar burning velocity measurements. The ignition vessel described in section 2.2 was modified slightly before being used for the BV measurements (Figure 2). The refrigerant + air mixture, prepared in the gas mixing setup, flowed through the ignition vessel from the bottom to purge the system (displacing at least eight times the vessel's volume). Then, the gas inlet and outlet were closed for two minutes to stabilise the fluid inside the vessel before opening the gas outlet to the expansion tank followed by the ignition of the mixture at the top cap (the ignition cap). The resulting flat flame propagated downward while a high-speed camera recorded the propagation. The BV of the mixture is equal to the lower luminous boundary of the flat flame's propagation speed [23]. The pressure inside the vessel was kept near atmospheric by opening the exhaust line to the expansion tank. The corrosive combustion products were neutralised by passing them through a soda-lime tower and NaOH solution in the neutralisation section (as described in the SI).

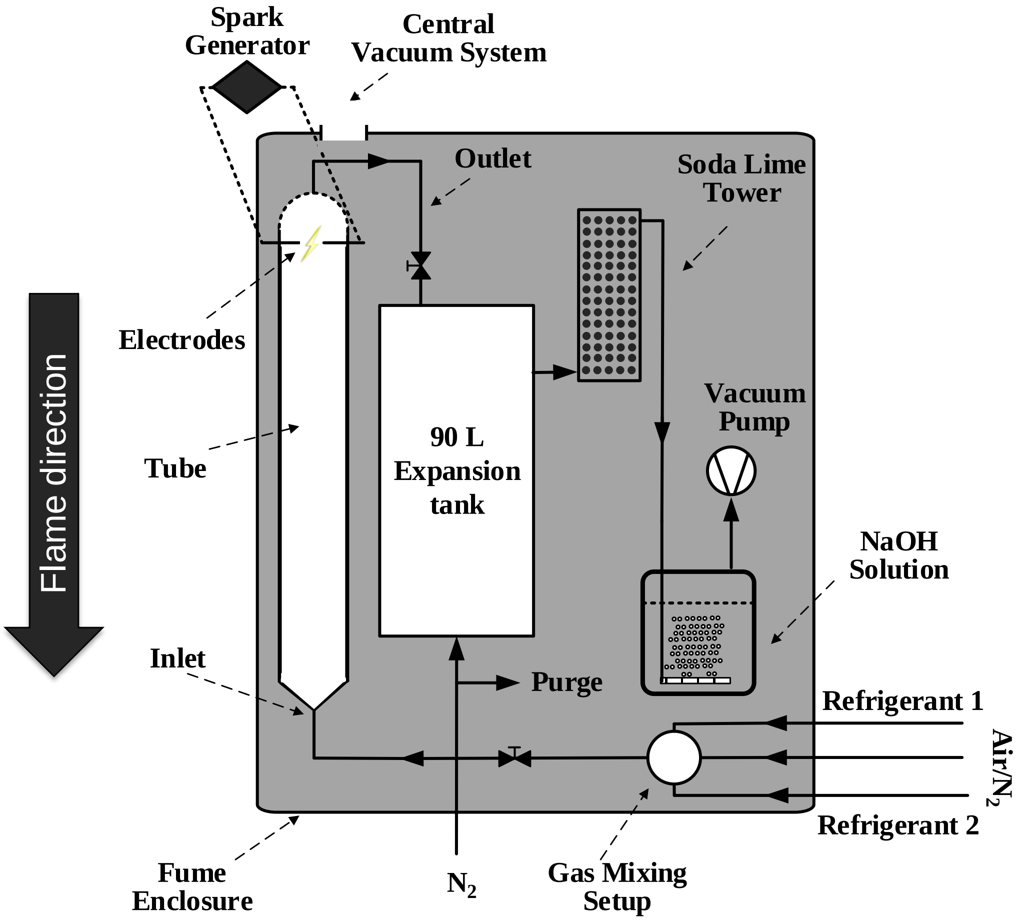


Figure 2: Schematic of the flat flame method configuration for the measurement of laminar burning velocity.

3. Results and Discussion

3.1 Minimum Ignition Energy

Pure Refrigerants

The MIE of the refrigerant/air mixtures was measured against the equivalence ratio to determine the lowest energy required to ignite the mixture, which the equivalence ratio is defined as follows:

$$\varphi = \frac{(\text{Refrigerant/Air})}{(\text{Refrigerant/Air})_{Stoichiometiric}} \qquad (1)$$

The equivalence ratio is used to indicate whether the combustion is stoichiometric ($\varphi = 1$), lean with excess air ($\varphi < 1$) or rich with incomplete combustion ($\varphi > 1$). Figure 3 (a) shows the measured MIE of R717 at equivalence ratios from 0.7 to 1.2. The lowest MIE was found to be (18.0 ± 1.4) mJ at an equivalence ratio of 0.9. The MIE values for R32 – measured at three equivalence ratios between 1 and 1.4 – are illustrated in Figure 3 (b), with the lowest ignition energy of (8.0 ± 1.5) mJ at an equivalence ratio of 1.27. As shown in Figure 3 (c), the MIE of R1234yf was measured to be (510 ± 130) mJ at an equivalence ratio of 1.33. The lower MIEs of R32 shows that the risk of using it the working fluid in the cooling systems is significantly higher than the HFO, R1234yF, or even R717 given the toxic combustion products. Figure 4 shows the propagating flame during the MIE measurement for refrigerant/air mixtures of R717, R32 and R1234yf.

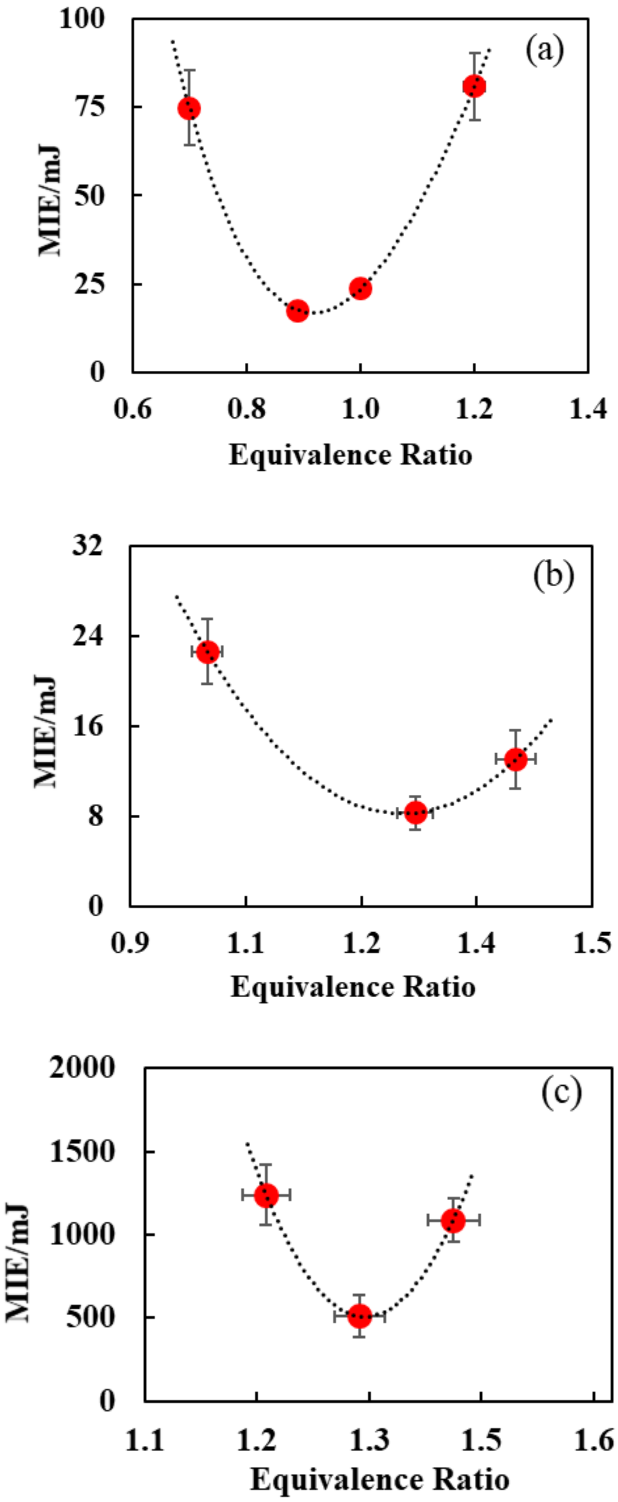


Figure 3: The MIE of R717 (a), R32 (b) and R1234yf (c) at different equivalence ratios.

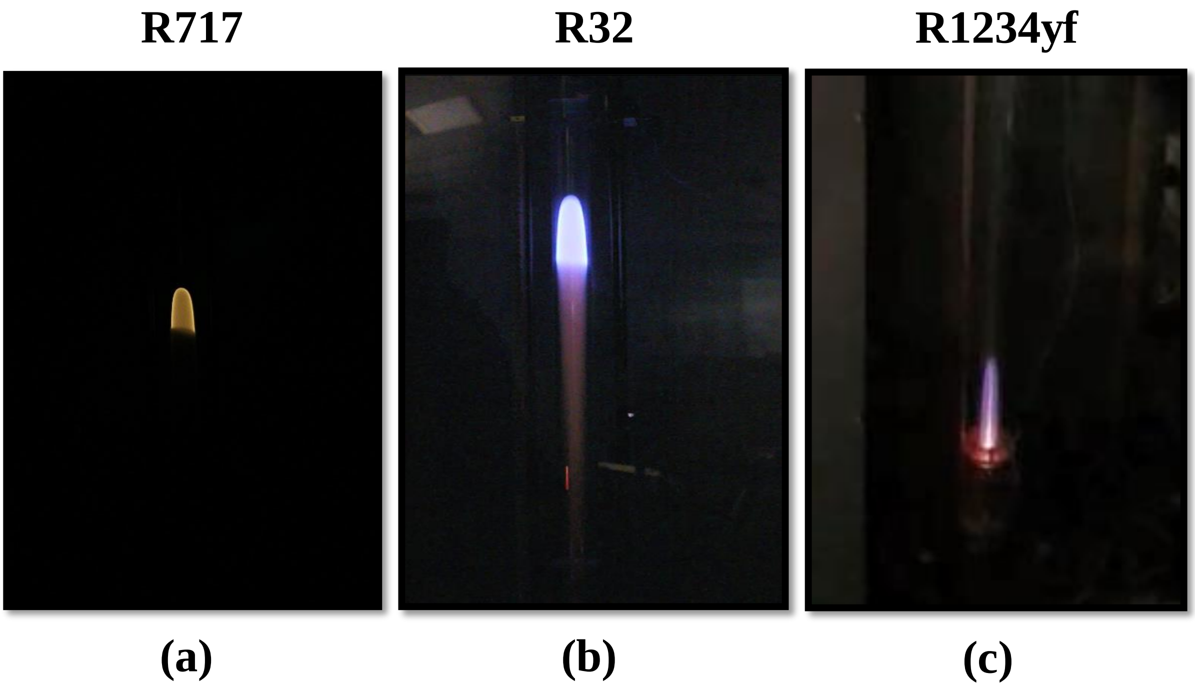


Figure 4: The propagating flame during MIE measurement of refrigerant/air mixtures for (a) R717, (b) R32 and (c) R1234yf.

A wide variation in reported MIEs for the refrigerants in the literature points to the dependency of this property on the measurement characteristics such as the spark gap and duration [20]. Takizawa et al. [14] conducted a comprehensive study of MIE measurements for mildly flammable mixtures. They used an alternative method based on quenching distance in which the minimum distance between two surfaces that allowed a self-sustained flame propagation to take place was determined. Movileanu et al. [28,29] employed a similar approach to measuring the minimum ignition energies for hydrocarbon/air mixtures. Here, we compare the MIEs measured in this work with those reported by Takizawa et al.[14] by determining an equivalent quenching distance using the following equation:

$$E_{min} = \left(\frac{1}{6}\right)\pi d_{min}^{3}\rho_b c_p (T_b - T_u) \tag{2}$$

Here d_{min}, ρ_b, c_p, T_b and T_u stand for the minimum quenching distance, the burned gas density, the burned gas heat capacity, the burned gas temperature, and the unburned gas temperature, respectively. T_b is considered equivalent to the adiabatic temperature of the flame, where the adiabatic flame temperature is determined by chemical and thermodynamic equilibrium reached in the burned gas. The values reported for ρ_b, c_p, T_b and T_u by Takizawa et al. [14] were used in Equation (2). for d_{min} is measured by reducing the flame thickness from the measured quenching distance between two surfaces (quenching plates equipped on the electrodes), as expressed below:

$$d_{min} = (d_q - 2\delta) \tag{3}$$

where d_q and δ denote the measured quenching distance and flame thickness, respectively. Takizawa et al. [14] estimated the MIE of R717 at an equivalence ratio of 1 to be 19 mJ, with a quenching distance of 7.45 mm. At the same equivalence ratio, our measured MIE for R717 (24 mJ) corresponds to a quenching distance of (7.75 ± 0.15) mm, which is within 4% of the quenching distance reported by Takizawa et al. [14]. The corresponding quenching distance for the MIE of R32 measured in this work at an equivalence ratio of 1.27 (8 mJ) is (5.8 ± 0.2) mm. Takizawa et al. [14] reported the MIE for R32 at this equivalence ratio to be 14 mJ based on their measured quenching distance of 6.45 mm. Although this difference is larger than for R717, the agreement between the two independent determinations is reasonable.

The measured MIE for R1234yf – (510 ± 130) mJ – corresponds to a quenching distance of (23 ± 1) mm at 23 °C. Takizawa et al. [14] reported a quenching distance for R1234yf around 25 mm, corresponding to MIE of approximately 550 mJ. Again this level of agreement is encouraging. However, the MIE for R1234yf was also found in this work to be particularly sensitive to ambient temperature, with MIEs measured at 17 °C in the range of 3-4 J, six to eight times larger than MIEs at 23 °C. No dependence of the MIE on ambient temperature was observed for R32.

The sensitivity of the MIE to different spark gap sizes was also studied. Figure 5 shows the MIE of R32 at spark gaps of 5 and 6.5 mm. The MIE of R32 at the spark gap of 6.5 mm was measured to be 8 mJ at an equivalence ratio of 1.27. This increased to 31 mJ for a 5 mm spark gap because of the excessive flame heat loss to the electrodes and shortage of radicals, which increased the ignition energy by four times. Further increase in the spark gaps led to unsuccessful sparks, preventing from measuring the MIE with larger gaps. The increasing pattern of the MIE by reducing the spark gap is in consistent with trends reported in the literature [22].

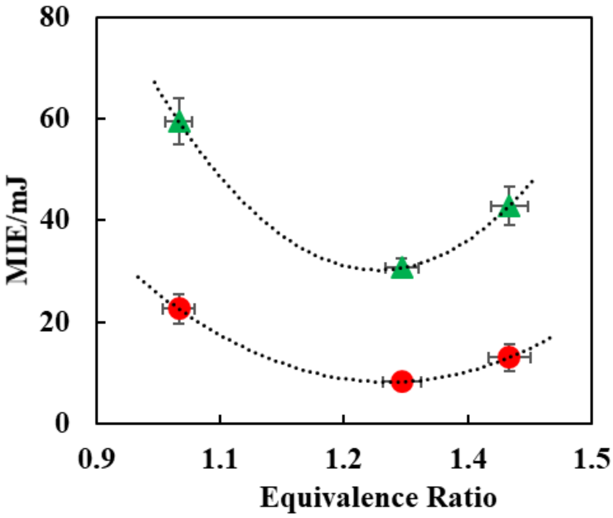


Figure 5: Effect of spark gap size on the MIE of R32: ● 6.5 mm gap and ▲ 5 mm gap.

Refrigerant mixtures

After validation of our measurement system by determining the MIEs of pure refrigerants, the effect of adding non-flammable refrigerants like R744, R125 and R134a on the MIE of mixtures of R32 and R1234yf was investigated. The minimum ignition energy of a ternary mixture of R32 + R1234yf + R744 (28:66:6 wt%) was measured at concentrations of 12, 14, and 16 vol% in air (Figure 6). The lowest value occurred at a concentration of 14 vol% with the corresponding MIE of (330 ± 60) mJ, which is 40 times higher than the MIE of pure R32. This mixture requires more energy to generate a self-sustaining flame kernel that would continue to propagate after the spark discharge.

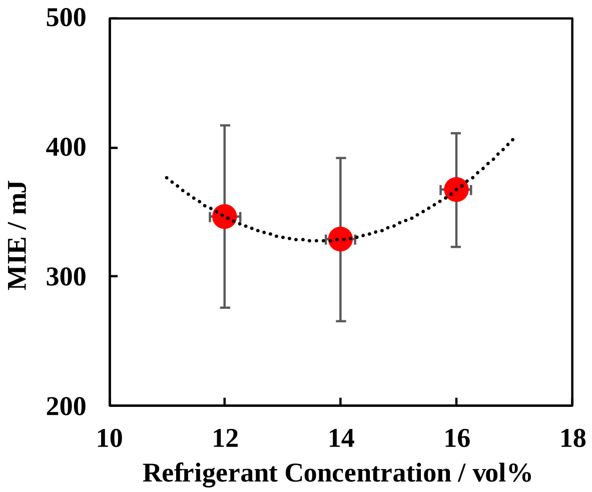


Figure 6: The MIE of R32 + R1234yf + R744 (28:66:6 %wt) mixture at different concentrations (vol%) in air.

In this work, neither a four-component equimolar mixture of (R32 + R1234yf + R134a + R125) at refrigerant concentrations of 25, 27 and 29 vol% in air nor the equimolar five-component mixture of (R32 + R1234yf + R134a + R125 + R744) at similar concentrations could be ignited, even when the mixture was exposed to 8 J of spark energy. This shows the extinguishing effect of R134a, R125 and R744 on the R32 and R1234yf, which makes the mixture less risky to the ignition sources. For the five-component mixture the ignition risk threshold concentration of R1234yf found by increasing it sequentially to 80 vol%, with the other four components held at the same ratio (down to 5 vol%). At refrigerant concentrations of 12 and 15 vol% in air this mixture could be ignited with MIEs of (4.4 ± 0.8) J and (3.8 ± 0.8) J, respectively. Table 4 presents a summary of the MIEs measured for the multi-component mixtures. Also, the flames produced at these concentrations were weak and only propagated around 5 cm along the tube – less than the 30 cm threshold defined by EN1839 [26] as the minimum propagation distance required for a successful ignition. Such a high MIE and weak flame propagation emphasise the significance of blending refrigerants in alleviating the ignition hazards associated with cooling systems.

Table 4: The MIE of multi-component mixtures of refrigerants.

Mixture	Refrigerant/vol%	MIE/J
0.25 R1234yf + 0.25 R32 + 0.25 R134a + 0.25 R125	25, 27 and 29	No ignition (up to 8)
0.2 R1234yf + 0.2 R32 + 0.2 R134a + 0.2 R125 + 0.2 R744	25, 27 and 29	No ignition (up to 8)
0.8 R1234yf + 0.05 R32 + 0.05 R134a + 0.05 R125 + 0.05 R744	12	4.4 ± 0.8
0.8 R1234yf + 0.05 R32 + 0.05 R134a + 0.05 R125 + 0.05 R744	15	3.8 ± 0.8

3.2 Laminar Burning Velocity

Pure Refrigerants

Several attempts to measure the laminar burning velocity of R32 and R1234yf were also made using the Bunsen burner approach. However, it was not possible to maintain a stable flame with the tested refrigerants unless the oxygen concentration of the air was increased to 28 % for R32 and 44.5 % for R1234yf. This confirms that the Bunsen burner is not applicable for measuring the burning velocities of 2L refrigerants such as R32 and R1234yf with air [21].

The vertical tube method was used for the BV measurements of R32 and R1234yf, as explained in the SI. However, based on Equation (SI-7) and Figure SI 5, calculation of the flame area is one of the critical sources of uncertainty for a luminous flame, because the accurate determination of the flame boundary is a difficult task. Figure 7 shows the flame propagation of an R717/air mixture at an equivalence ratio of 1.1 in the vertical tube. The area of the flame varies by 50 % along the tube while the flame propagation speed was essentially constant (around 25 cm/s).

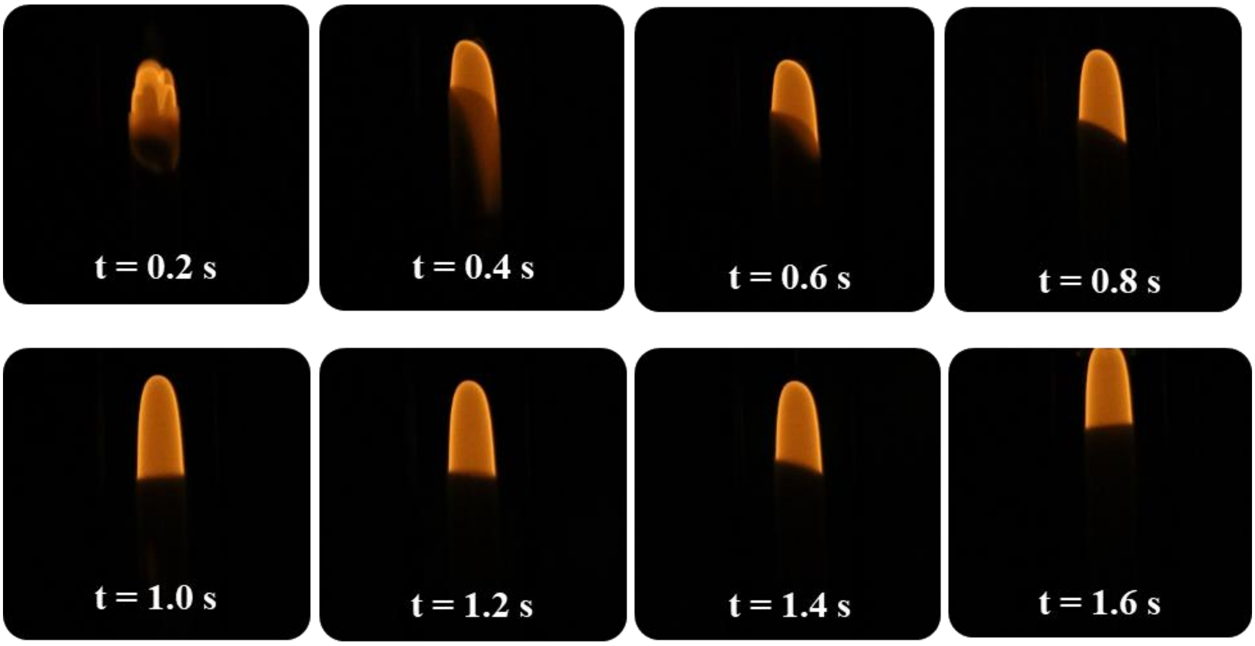
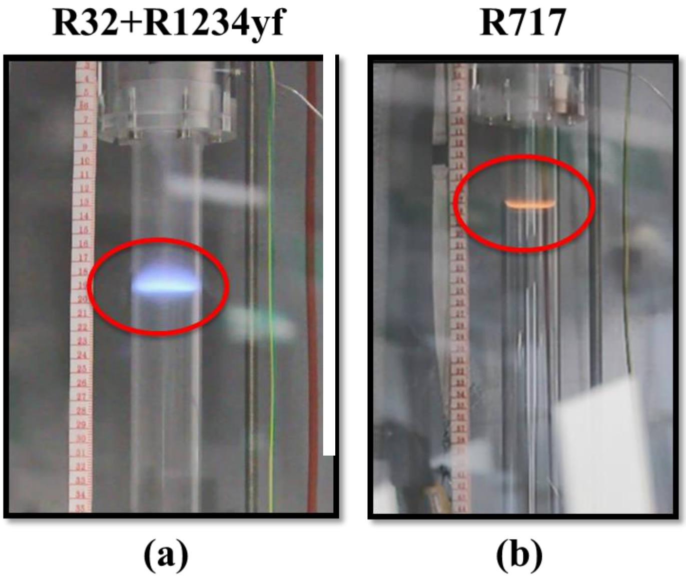


Figure 7: Flame propagation of R717 in the vertical tube method (equivalence ratio of 1.1).

Accordingly, the measurement system was modified by moving the ignition cap from the bottom to the top of the vessel to enable use of the flat flame method and overcome problems associated with buoyancy. The flame produced in this approach was a one-dimensional surface that propagated downward with a velocity equal to the laminar burning velocity of the mixture [23]. Figure 8 illustrates the flame propagation achieved using the flat flame approach for a mixture of R32 + R1234yf (95:5 vol%) and pure R717.



R32+R1234yf R717

(a) (b)

Figure 8: Flat flame propagation of (a) 0.95 R32 + 0.05 R1234yf and (b) pure R717.

Table 5 presents the measured BVs for R32 and R717 with the flat flame method, together with some results from the literature [10,11,13,24,30,31]. The laminar burning velocity of R717 at an equivalence ratio of 1.1 was measured to be (8.4 ± 0.4) cm/s using the flat flame method. At the similar equivalence ratio, the laminar burning velocity of R717 was reported to be between 6.7 cm/s [30] and 8 cm/s [31] based on measurements using the cylindrical bomb method. The laminar burning velocity for R32 at an equivalence ratio of 1.1 was measured in this work with a 50 mm diameter tube to be (7.4 ± 0.3) cm/s, which is in excellent agreement with the results of Takizawa et al. [10], where a value of 7.3 cm/s was reported using the vertical tube method. The results obtained via the flat flame method typically exhibit a dependence on the tube diameter; using a 40 mm diameter tube, we measured a laminar burning velocity of (6.4 ± 0.3) cm/s for R32 at an equivalence ratio of 1.1. Takizawa et al. [11] also used a vertical tube with a 40 mm diameter and measured the laminar burning velocity of 6.3 cm/s for R32 at a similar equivalence ratio.

The laminar burning velocity of R1234yf could not be measured because the flame was profoundly affected by buoyancy effects even in the flat flame method configuration: the induced convective currents in the tube prevented the flame from propagating downwards. Measuring the laminar burning velocity of R1234yf via the flat flame method might thus require microgravity conditions [13].

Table 5: Burning velocities of various pure components obtained with different methods and apparatus.

Refrigerant	Equivalence Ratio	Method	Tube ID/mm	BV/cm.s^{-1}	Ref.
R717	1.1	Heat Flux	-	6.3	[32]
	1.1	Cylindrical Bomb	-	6.7	[30]
	1.1	Vertical Tube	40	7.3	[24]
	1.1	Spherical Flame	-	7.5	[33]
	1.1	Cylindrical Bomb	-	8.1	[31,34,35]
	1.1	Flat Flame	50	8.4 ± 0.4	This work
R32	1.1	Vertical Tube	60	7.3	[10]
	1.1	Flat Flame	50	7.4 ± 0.3	This work
	1.1	Flat Flame	40	6.4 ± 0.3	This work
	1.1	Vertical Tube	40	6.3	[11]
R1234yf	1.33	Microgravity	-	1.5	[13]

Refrigerant mixtures

Determination of the laminar burning velocity of R32 + R1234yf and R32 + R1234yf + R744 mixtures were also attempted. No propagation could be established using the flat flame method for the R32 + R1234yf + R744 (28:66:6 wt%) mixture at refrigerant/air concentrations between 12 to 16 vol%. Even using the vertical tube method, no laminar flame propagation was observed. These results are consistent with the findings for pure R1234yf and are reasonable, considering R1234yf is the dominant component in these mixtures. Based on this, a BV value for R1234yf (1.5 cm/s) could be used as a rough estimate of the mixture's laminar burning velocity.

To cast light on the effect of adding R1234yf to R32 on the BV, binary mixtures of R32 + R1234yf at 19 vol% in air were studied. The laminar burning velocity of pure R32 at this refrigerant concentration in air was measured to be (7.4 ± 0.3) cm/s using the flat flame method with a 50 mm diameter tube. The laminar burning velocity for a mixture of R32 + R1234yf containing 5 vol% of R1234yf was then measured to be (6.6 ± 0.3) cm/s. No flat flame propagation could be maintained for a mixture containing 10 vol% R1234yf, indicating that the laminar burning velocity of such a mixture is below 5 cm/s. The minimum laminar burning velocity measured via the flat flame method in this work was 5 cm/s for an R717/air mixture at an equivalence ratio of 0.95), as summarised in Table 6.

Table 6: Measured burning velocities of refrigerant mixtures in air.

Mixture	Refrigerant/vol%	Method	BV/cm.s^{-1}
R32 + R1234yf + R744 (28:66:6 wt%)	12 to 16	Flat flame	< 5
R1234yf + R32 (5:95 vol%)	19	Flat flame	6.6
R1234yf + R32 (10:90 vol%)	19	Flat flame	< 5**

* The literature BV value for pure R1234yf (1.5 cm/s) provides a rough estimate of the mixture's BV.

** Lower limit of the measurable BV with the apparatus.

4. Conclusions

Two pieces of new apparatus were designed, commissioned and deployed to measure the minimum ignition energy and laminar burning velocity of environmentally-friendly refrigerant mixtures. The MIEs of R717, R32 and R1234yf were measured to be (18.0 ± 1.4) at an equivalence ratio of 0.9, (8.0 ± 1.5) mJ at an equivalence ratio of 1.27 and (510 ± 130) mJ at an equivalence ratio of 1.33, respectively.

To reduce the ignition risk, R1234yf and R744 were added to the R32/air mixture, which resulted in a substantial rise in the MIE to 0.33 ± 0.06 J at 14 vol% in air. Adding non-flammable refrigerants of R134a and R125 to R32 and R1234yf (an equimolar four-component mixture) removed the flammability of the blend. An equimolar five-component mixture of (R32 + R1234yf + R134a + R125 + R744) could not be ignited at concentrations from 25 to 29 vol% in air with spark energies up to 8 J. To ignite the mixtures, it was necessary to increase the amount of R1234yf in the five component mixture to 80 vol%, and then apply MIEs of (4.4 ± 0.8) J and (3.8 ± 0.8) J for concentrations of 12 vol% and 15 vol% in air, respectively.

The BV of R32 was measured to be 6.4 cm/s and 7.4 cm/s at an equivalence ratio of 1.1 with 40 and 50 cm tube IDs. No propagating flame could be established for R1234yf, precluding the determination of its BV. By adding 5 vol% of R1234yf to the R32/air mixture at 1.1 equivalence ratio, the laminar burning velocity decreased by 0.8 cm/s. However, no propagating flames could be established for R1234yf + R32 mixtures containing 10 vol% R1234yf, indicating that laminar BV for mixtures with 10 vol% or more R1234yf is below the measurable threshold of 5 cm/s.

Mixtures rich with R1234yf and R744 could provide more sustainable refrigerant solutions as both have very low global warming potential. This study provided the MIE of those mixtures at zero humidity level and room temperature. However, the flammability of R1234yf varies significantly by temperature and humidity. In future work, a certain threshold value for R744 within a mixture of R1234yf/air at different humidity levels and temperatures needs to be determined; a concentration above which the MIE energy is high enough that the mixture is considered non-flammable at various weather conditions across the globe. Also, the rate of pressure rise and its maximum value caused by explosion for different scale of refrigerant mixtures should be investigated to address the effect of the confinement as well as the extent of the hazards in case of ignition.

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