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## Fractionation, release testing and flammability evaluation of novel refrigerants comprising R-744 and fluorocarbons

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### ABSTRACT

As the world becomes more focused on climate change, there is growing willingness to bring about rapid reduction in emissions of greenhouse gases. Refrigerants and blends are used throughout the world in a wide range of applications from agriculture, shipping, automotive and medical. There is a drive from each sector to identify new lower GWP (global warming potential) alternatives to replace currently used fluids while at the same time ensuring that performance and safety are acceptable. Many applications are now using or evaluating flammable fluids as a means of achieving GWP reduction while staying close to the properties of existing refrigerants. However, some applications still require non-flammable fluids. This study has identified several non-flammable carbon dioxide (CO<sub>2</sub>) rich blends that offer potential as replacements for existing fluids while maintaining excellent thermodynamic properties. Two of these blends are R-473A and LFR3. This paper will present the results of studies conducted on fractionation (vapor leakage) of these fluids from systems to determine actual compositions during the leak process over a wide range of ambient temperatures. These compositions were subjected to ASTM E681<sup>[1]</sup> flammable limit determination testing to assess whether leakage from a system could ever generate a flammable composition. Modelling of the leakage experiments with the NIST REFLEAK<sup>[2]</sup> software will also be presented. A novel flow apparatus has been developed to study what happens when high-pressure refrigerants containing R-744 are expanded to atmospheric pressure. This is relevant in understanding phase behaviour when refrigerant is released by pressure relief valve or pipe failure and when liquid refrigerant is expanded in a refrigeration cycle to low evaporator pressures. Results quantifying the flash vapor formation and dry ice formation will be presented.

### 1. INTRODUCTION

There are many challenges within the refrigeration sector that need to be overcome to bring about the change required to achieve the F-gas regulation timetable<sup>[3]</sup> and other regulations around the world covering hydrofluorocarbon (HFC) phase-down. There is a need to adopt new fluids of lower GWP less than 300 while maintaining high energy efficiency and product performance that will drive down emissions of greenhouse gases. For decades, the current portfolio of fluids has been used in a wide range of applications due to cost, availability, excellent thermodynamic properties, and system compatibility. Building customer confidence is vital and the key to removing the barriers currently in place which will help speed up the adoption of greener alternatives. The purpose of this paper is to highlight that novel CO<sub>2</sub> based fluids can be an integral part in reducing climate change. Not only are there significant environmental, performance, and economical saving to be expected, these fluids are developed to be dropped into existing systems leading to minimal disruption. Being green and economical are not the main drivers to developing new alternative fluids. The day-to-day practicalities of handling, transferring, shipping, use in systems (the life cycle of the fluid) are what will drive the change.

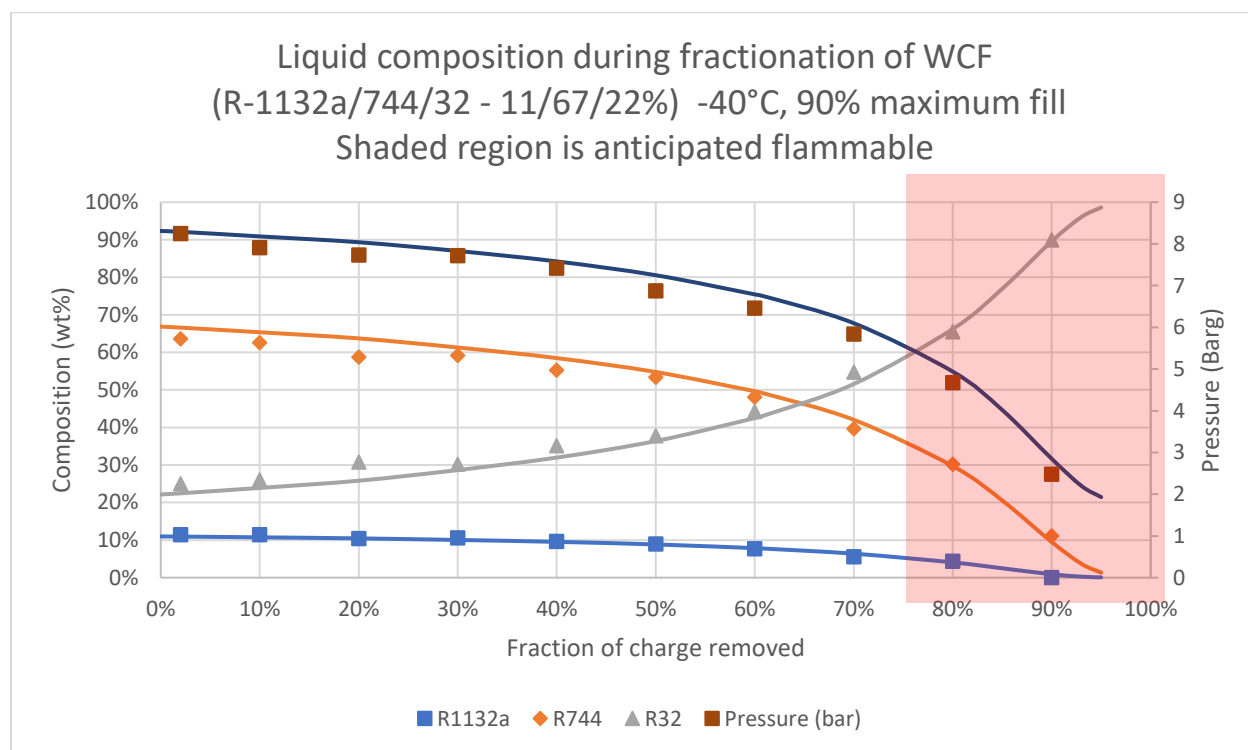
## 2. DATA MODELLING

### 2.1 Model generation

To aid the development of novel fluids a combination of data derived from experimental testing in conjunction with software packages are used to drive the research forward. The models in the software packages, particularly NIST REFLEAK rely on good high-quality data. This PTw (Pressure-Temperature-mass fraction) data has been generated on binary pairs using an in-house built apparatus. The data from this set up is regressed and fitted to generate binary interaction parameters (BIPS) which are incorporated into the models within the software.

### 2.2 Model validation

Experimental data is required to validate and support the model. With good agreement between the two sets of data the user can quickly screen a series of blend formulations and identify potential candidates to investigate further. A range of fractionation experiments have been conducted, varying composition, fill density and temperature of the LFR3 blend. The same experimental parameters were modelled in REFLEAK 5.1 using derived BIP's. The findings from the two techniques are summarized in Figure 1. The smooth lines are from REFLEAK and the individual points experimental data<sup>[4]</sup>. There is excellent agreement between the two trajectories of data providing the confidence and assurance required from a model.



**Figure 1:** Comparison of Modelled Liquid Compositions vs Experimental Fractionation of LFR3

## 3. FLAMMABILITY TESTING

### 3.1 Background

Flammability tests shall be conducted in accordance with ASTM E681. For classification of Class 2L, Class 2, or Class 1 materials, testing shall be in a nominal 0.424 ft<sup>3</sup> (12 L) spherical glass flask (Figure 2). The ignition source shall be a spark from a transformer secondary rated at 15 kV and 30 mA alternating current (A/C) as described in ASTM E681, with a 0.4 second spark duration. The electrodes shall be 0.04 in. (1 mm) diameter L-shaped tungsten wire electrodes that are spaced 0.25 in. (6.4 mm) apart and that extend out of the plane of the electrode holder (see

spark assembly diagram in Figure 3 for more details). The ignition source shall be placed at a height from the bottom of the test vessel that is one-third the diameter of the vessel. Tests shall be conducted at the temperature of 60°C initially and at 1% by volume (refrigerant/air) increments. The absolute humidity of the air used for mixing shall be 0.0088 g of water vapor per gram of dry air (which equates to 50% rh at 73.4°F [23.0°C] and 14.7 psia [101.3 kPa]).

Testing will be conducted on the worst-case formulation (WCF) and on the worst-case fractionated formulation (WCFF). The WCFF is determined by applying the method as described in ASHRAE standard 34 [5].

For an ASHRAE application seeking a Class 2L assignment additional information is required in the form of burning velocity (BV). ASHRAE research project report RP-1583 [6] (Assessment of burning velocity test methods) details what methods are available. There are three methods discussed, Schlieren, vertical tube, and  $\mu$ -g (spherical vessel) and assessed. For ASHRAE standard 34-2019 any of the methods can be used if they have been validated against R-32 and R-152a and can show the results fall within the tolerance levels. For R-32 this is 6.7 +/- 0.7 cm/s and R-152a 23.0 +/- 2.3 cm/s. Koura utilises the Jabbour method (vertical tube), and the setup is shown in Figure 6.

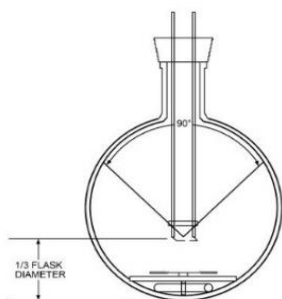


Figure 2: Test Apparatus

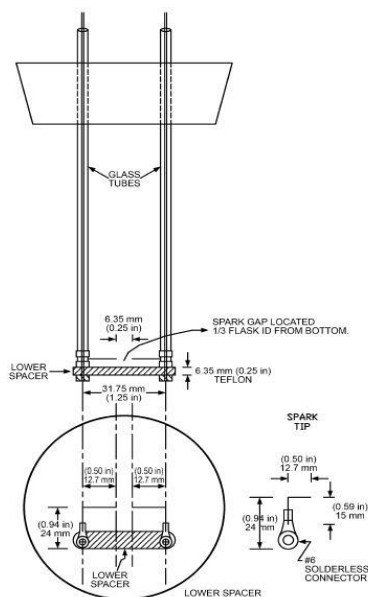


Figure 3: Spark Electrode Assembly

### 3.2 Experimental Design

The testing of refrigerants that contain fluorine in the molecule have additional safety challenges that need to be addressed. During propagation events hydrogen fluoride (HF) is released as a combustion product. HF is toxic and corrosive and is mitigated by a combination of local exhaust ventilation (LEV) and a scrubbing system to neutralise the HF. It also reacts with the glass test sphere causing etching which can impact on the results generated and leads to frequent replacement of flasks. Anko [7] have developed a system using a polycarbonate test sphere and a modified internal electrode system as shown in Figure 4. By using materials resistance to HF, maintenance is reduced, throughput of testing is increased, and costs are reduced.

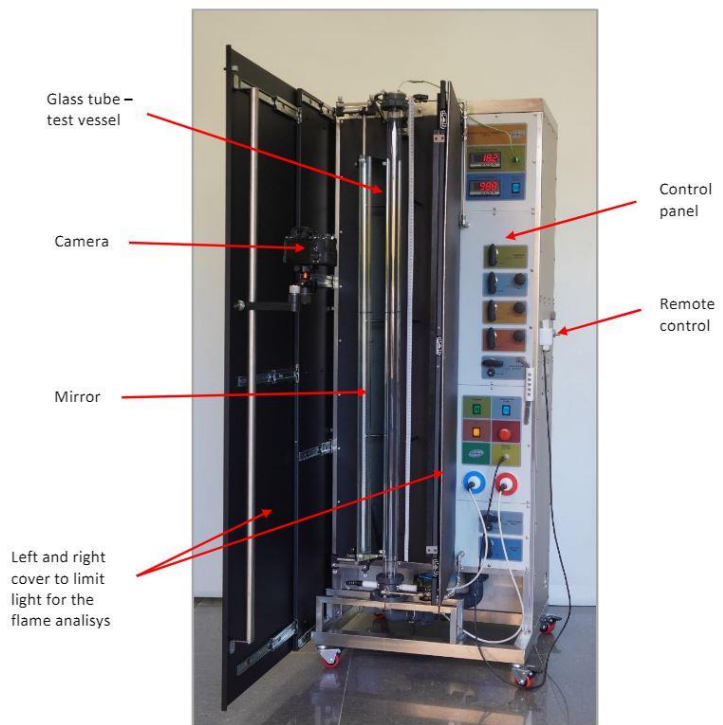


**Figure 4:** Polycarbonate Sphere and electrodes

The humidity of the air entering the test cell is controlled by using a saturated calcium nitrate tetrahydrate solution. This relies on the environmental conditions of temperature and humidity being stable so the required relative humidity (RH) of 50% can be achieved. To overcome the fluctuating laboratory conditions a humidifier apparatus (Figure 5) instead of salt solutions is utilized. This can control the temperature, humidity, and flow rate of the air via a series of mass flow controllers (MFC), thermocouples and a humidity sensing module. The tube exiting the instrument is heated to prevent condensation before the air enters the test cell.



**Figure 5:** Humidifying instrument



**Figure 6:** Burning Velocity (Jabbour method)

### 3.3 Design Validation

A series of test experiments using difluoromethane (R-32) and 1,1-difluoroethane (R-152a) were performed to validate the equipment before blend testing. The purity of the two components were >99.5 % w/w using gas chromatography (GC). These components have been studied and the experimental data published in the ASHRAE 34-2019 standard. A comparison of ASHRAE standard figures against data generated in the flammability limit test apparatus and burning velocity are given in Table 1 and Table 2, respectively.

**Table 1:** Flammability limits comparison data

| COMPONENT | ASHRAE      |             | KOURA       |             |
|-----------|-------------|-------------|-------------|-------------|
|           | LFL (v/v %) | UFL (v/v %) | LFL (v/v %) | UFL (v/v %) |
| R32       | 14.4        | 29          | 15.2        | 30.3        |
| R152a     | 4.8         | ---         | 4.84        | ---         |

The lower flammable limit (LFL) and the upper flammability limit (UFL) for the data sets are within acceptable tolerances.

**Table 2:** Burning velocity comparison data

| COMPONENT | ASHRAE    | Koura     |
|-----------|-----------|-----------|
|           | BV (cm/s) | BV (cm/s) |
| R32       | 6.7       | 6.5       |
| R152a     | 23        | 25        |

The data is within the required tolerances of +/- 0.7 cm/s for R-32 and +/- 2.3 cm/s for R-152a.

### 3.4 Flammability Data

As developed R-473A and LFR3 are non-flammable blends. The compositions of the two blends are summarized in Table 3 and Table 4, respectively. R-473A has been given an A1 classification by the ASHRAE SSPC34 committee.

**Table 3:** R-473A composition data

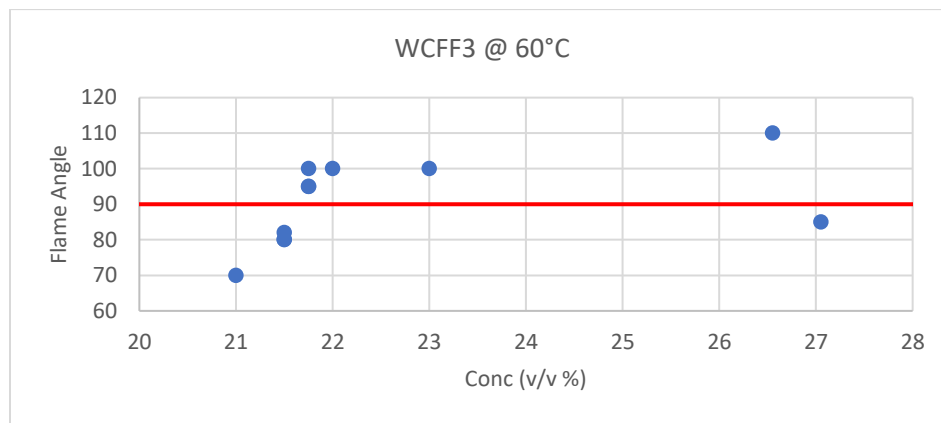
| Composition | R1132a / R23 / R744 / R125<br>By Mass % |
|-------------|---|
| Nominal     | 20.0 / 10.0 / 60.0 / 10.0               |
| WCF         | 20.5 / 9.0 / 61.5 / 9.0                 |
| WCF3        | 23.1 / 10.8 / 48.3 / 17.8               |

**Table 4:** LFR3 composition data

| Composition | R1132a / R32 / R744<br>By Mass % |
|-------------|----------------------------------|
| Nominal     | 10.0 / 21.0 / 69.0               |
| WCF         | 11.0 / 22.0 / 67.0               |
| WCF3        | 3.0 / 70.0 / 27.0                |

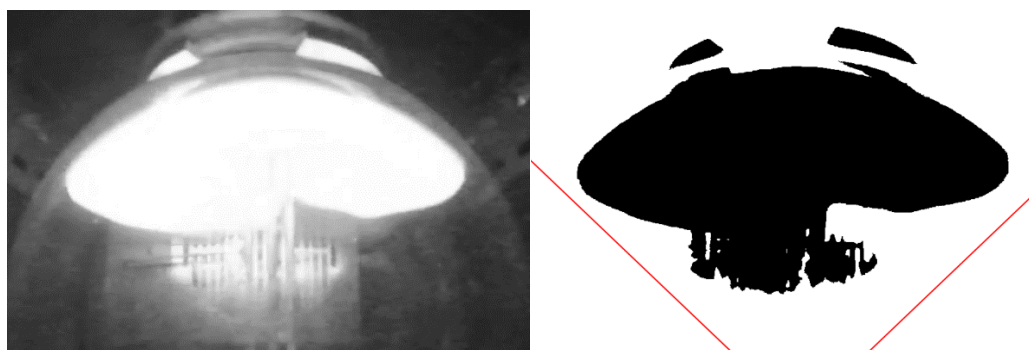
A package of work was conducted by a third party (DEKRA) <sup>[8]</sup> to investigate flammable limits and burning velocity (BV) on a range of LFR3 candidates. This data was verified internally using our flammability capability. The two data

sets for flammable limits have been combined and represented graphically in Figure 7. The blends for in-house testing were made up gravimetrically and analyzed on an Agilent 7890A GC using a thermal conductivity detector (TCD) and helium as a carrier gas. Each component was calibrated to produce a response factor which was converted to mass %.



**Figure 7:** Flammability limits for LFR3 WCFF3

The images for determining the flammable limits are captured using a high-speed camera operating at 60 frames per second (FPS). The light entering the camera (ISO) is adjusted to produce high quality images to support the image processing software. The software takes the image and reverses the color to white/black. This reduces background noise leaving behind the flame shape to process. The 90-degree angle is overlaid on the image from the ignition point as shown by the two red lines. The criterion for a flame propagation is described in the standard as any combustion that, having moved upward and outward from the point of ignition to the walls of the flask, is continuous along an arc that is greater than that subtended by an angle equal to 90 degrees, as measured from the point of ignition to the walls of the flask. Figure 8 shows the actual image and that after processing.



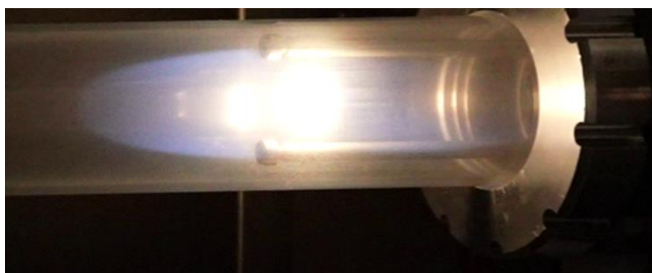
**Figure 8:** Flammability limits for LFR3 WCFF

The burning velocity of LFR3 WCFF3 was carried out internally. To determine the maximum BV of a flammable substance, the BV must be measured at several concentrations ranging from the LFL to the UFL. BV measurements are conducted starting from the LFL to above 125% of the stoichiometric concentration. Appendix F of ASHRAE standard 34 describes the process for determining stoichiometric combustion of multi component blends. The findings from the BV testing of LFR3 WCFF are summarized in Table 5.

**Table 5:** BV of LFR3 WCFF

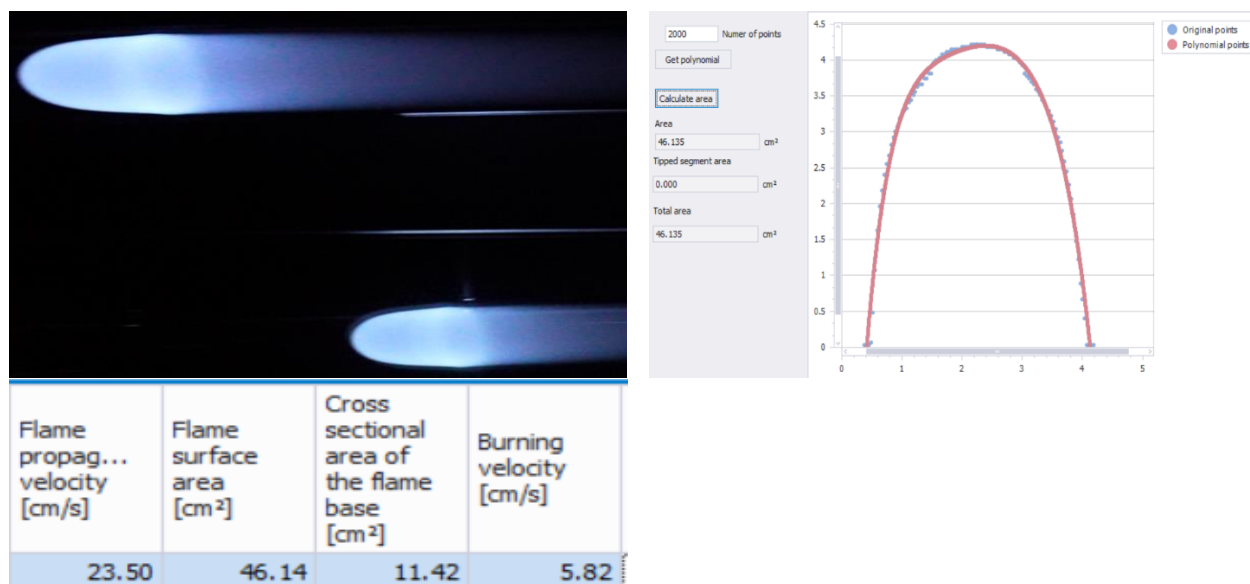
| Fuel Conc v/v % | BV (cm/s)   |
|-----------------|---|
| 21.92           | Small blue flame. No upward motion, BV < 4 cm/sec |
| 23.10           | Small blue flame. No upward motion, BV < 4 cm/sec |
| 24.20           | Small blue flame. No upward motion, BV < 4 cm/sec |
| 27.20           | Small blue flame. No upward motion, BV < 4 cm/sec |

From the results it appears that LFR3 WCFF does not have a BV. The recording of the flame when viewed frame by frame shows an initial combustion event, followed by the development of a flame front with no upward propagation (Figure 9) then it goes out. This series of events occurs in less than a second. With the vertical tube method there are limitations on its ability to determine the BV of slow burning fuels. Around 4 cm/s is the limit for this type of apparatus as the BV is affected by a buoyant gas bubble just behind the flame tip. In practice the gas bubble deprives the flame tip of heat and decreases its temperature. This explains the extinction process observed for LFR3. With this knowledge we will report the BV of LFR3 as <4 cm/s.

**Figure 9:** BV of LFR3 with no upward propagation

The burning velocity is determined in a comparable way to the LFL. A Sony A7siii mirrorless camera recording in 4K at 100 fps is used to capture the flame. The image appears as two flames. The bottom image is from a mirror located to the left of the vertical tube angle at 45 degrees. This is used to observe the back of the flame to see if it is tipped. A tool within the processing software converts the number of pixels to a distance (1 cm). A series of images are taken once the flame is stable to determine the flame propagation velocity. Two other parameters required to find the BV are, flame front area and the cross-sectional area of the flame base. Jabbour's method<sup>[9]</sup> describes in detail the mathematics and equations involved to determine these parameters. The processing software has these equations built into it streamlining the operation to find the BV. Figure 10 below describes the process of determining the BV. Firstly, capture the image, carry out some image processing then calculate the BV





**Figure 10:** Images from camera and software for BV analysis

This study is proposing LFR3 for dual classification by the ISO 817 committee. The most flammable WCFF for LFR3 is 99% R32 and 1% CO<sub>2</sub>, essentially the same as R32 from flammable limits and BV considerations. Even once the leak path crosses the flammable boundary the burning velocities are very low, and the flammable region is very small. Only in extreme unrealistic scenarios could LFR3 achieve a flammable atmosphere. E.g., in an automotive air conditioning system over 90% of the charge would need to leak as a vapour at -40°C to leave behind a flammable composition of 98% R32. The vapour exiting the system during this period will always be non-flammable. Under these conditions the R32 would be present at <5% of the initial contents of a system. An automotive system typically has a fill density of 300 Kg/m<sup>3</sup>. This fill density was modelled in REFLEAK at three temperatures, -40, -20 and 0°C. Once the flammable region is reached it is anticipated at temperatures -20°C and above there will be no liquid left in the system, just vapour.

## 4. CRITICAL FLOW

### 4.1 Background

When fluid flows through a contraction (an orifice or a relief valve) the pressure drops, and the fluid expands. If the ratio of upstream to downstream pressures is more than about 2:1 then this results in choked flow (where the flow rate is not affected by changing the downstream pressure). Expansion of a non-ideal vapour or a supercritical fluid can result in the fluid entering the two-phase region as it drops in pressure. There is also a decrease in temperature as the fluid expands. This could lead to 'dry ice' being generated (solid CO<sub>2</sub> formation) as you approach the critical point. Understanding this behaviour will enable systems to be designed to mitigate this affect.

### 4.2 Experimental

The purpose of this experiment was to understand first, visually what happens to liquid CO<sub>2</sub> when it expands across an orifice plate. LFR3 and 473A have a similar density and critical point to CO<sub>2</sub> so the operation of these systems would be operated like CO<sub>2</sub>. The complexity of the experiments will be increased to understand the thermodynamic properties of the fluids, validate the model, how to deal with anticipated very cold temperatures downstream of an orifice, control dry ice formation, and consider the potential of generating flammable vapours if CO<sub>2</sub> separates out as a solid.



The data and information generated so far can be used to form the basis of relief valve sizing and downstream pipework, at the same time giving confidence that in the event of a pipe rupture or relief event the composition exiting is non-flammable.

#### 4.4 What next?

Iterations of the original setup are being developed to fine tune the model, mitigate solid CO<sub>2</sub> formation downstream (back-pressure control) and increase knowledge on flammable boundaries. Results and findings will be presented at a later date.

## 5. CONCLUSION

- LFR3 as formulated is non-flammable
- Leakage scenarios using REFLEAK can be accurately modelled with enhanced BIP's
- BV and flammability limits can be accurately defined of novel CO<sub>2</sub> based blends
- Phase behavior can be predicted using MATLAB models
- Visualization experiments with quantitative analysis support non-flammability of LFR3 during relief events

## REFERENCES

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- <sup>[2]</sup> Domanski, P. and Brown, J. (2016), REFLEAK: NIST Leak/Recharge Simulation Model for Refrigerant Blends, Version 5.0, Natl Std. Ref. Data Series (NIST NSRDS)
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- <sup>[5]</sup> ANSI/ASHRAE Standard 34-2019 - Designation and Safety Classification of Refrigerants
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- <sup>[10]</sup> Robert Low -Extending the range of performance of R-744. PAPER ID: 1042 DOI: 10.18462/iir.HFO.2021.1042