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Vanessa Webster

Ira Saxena

Robert Elliott Low

Christopher Seeton

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## **Fractionation testing for Low Critical temperature Blends**

**Vanessa WEBSTER\*, Ira SAXENA, Robert E. LOW, Christopher J. SEETON**

Research & Development Dept, Koura Global, The Heath Business & Technical Park, Runcorn, WA7 4QX, UK

+44 (0) 1928 518917 [vanessa.webster@kouraglobal.com](mailto:vanessa.webster@kouraglobal.com)

+44 (0) 1928 518921 [ira.saxena@kouraglobal.com](mailto:ira.saxena@kouraglobal.com)

+44 (0) 7825776801 [bob.low@kouraglobal.com](mailto:bob.low@kouraglobal.com)

+1-281-682-7898 [chris.seeton@kouraglobal.com](mailto:chris.seeton@kouraglobal.com)

\*Corresponding Author

### **ABSTRACT**

In a world that is focused on improving the environment and becoming a greener and more efficient planet the importance for change and development is ever increasing. To ensure that we are all doing our part to reduce global warming (GWP) and increase our performance and efficacy, we have developed refrigerant blends with R-744 as the principal component. While these blends are formulated to maximise performance whilst maintaining a low GWP, they are blends and may suffer from composition shifting if not properly handled in application. Fractionation studies with various formulations were carried out to ensure these blends maintain a non-flammable rating in application even as the composition in the working system may shift. Using experimental and modelled data to validate the opinion that when LFR3 is used in a system under different conditions it is unlikely to ever achieve a flammable scenario.

### **1. INTRODUCTION**

Fractionation is the change in composition of a blend when one or more of the components are lost or removed earlier/faster than the other(s). There are two basic behaviors of refrigerant molecules which explain why fractionation occurs.

1. Pure refrigerants exert pressure on the cylinder/system because the molecules are moving around. These movements increase with increasing temperature hence more pressure and decrease at low temperature, so lower pressure. Different refrigerants have different energies at same temperature therefore generate higher or lower pressure.
2. Refrigerant molecules constantly move from liquid to vapor and vapor to liquid at the surface of the liquid. At equilibrium, liquid and vapor transfer the same number of molecules back and forth. Boiling liquid transfers more from liquid to vapor and condensing vapor transfers more from vapor to liquid. Different refrigerants transfer back and forth to the vapor at different rates.

When temperature glide is high the refrigerants can separate during evaporation or condensation. This changes the composition of the resulting vapor and liquid. This composition separation is called fractionation. Multi component blend refrigerants when used in systems give users the concern of fractionation occurring and shifting in the system to decrease the efficiency and to potentially create a fluid that may become flammable and cause safety issues for the user. While fractionation does not normally occur in operating (running) systems, during periods of shutdown, fractionation may occur depending on leak location. Ensuring safety for users is of the utmost importance when using our products, so rigorous testing and modelling has been carried out to ensure full understanding of these conditions.

### **2. OVERVIEW**

To comply with current and impending national and international environmental regulations restricting the use and disposal of conventional CFC and HCFC refrigerants which contribute to global ozone depleting effects, the HVAC

industry is vigorously evaluating and testing HFC refrigeration blends. Blends have been developed with CO<sub>2</sub> as the basis to reduce the GWP and increase the performance and efficiency. While blends offer performance, capacity, and operational advantages there are significant possible service and operational issues associated with them. These issues occur due to fractionation of the blends.

For classification of a refrigerant blend as non-flammable by ASHRAE Standard 34<sup>1</sup> (Class 1 rating) the testing requires consideration of two compositions

- a) “Worst case formulation” (WCF)- the composition that is derived from adjusting manufacturing tolerances to maximize the flammable component concentration in the mixture
- b) “Worst case fractionation for flammability” (WCFF)- the composition with the highest concentration of flammable component(s) following a series of specified leakage analyses constituting vapor leaks from cylinders (not system leaks).

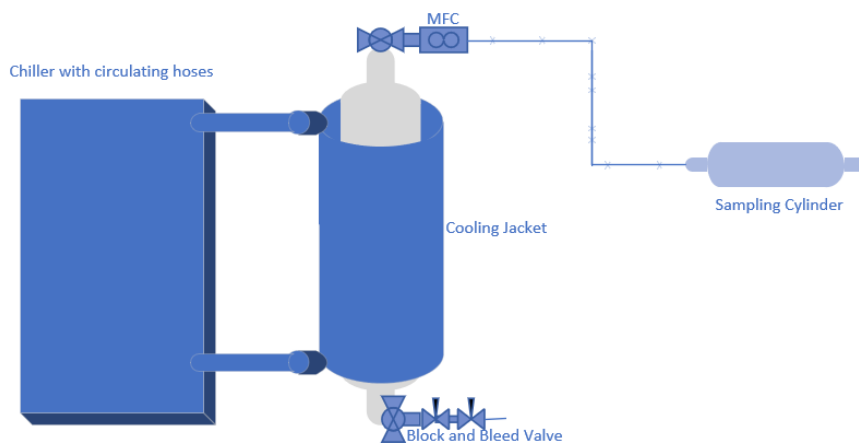
We have developed the following two blends:

Blend 1: R473A (R-1132a/23/744/125 with composition 20.0/10.0/60.0/10.0) and

Blend 2: LFR3 (R-1132a/32/744 with composition 21/10/69) which were studied for fractionation analysis.

### 3. EXPERIMENTAL SYSTEM

A typical fractionation apparatus consists of a 1000-ml stainless steel cylinder equipped with a dip tube, needle valves with sampling ports, a constant temperature environment, chiller, PTFE high pressure hose, and an electronic gas mass flow meter for vapor removal rate. A balance and computer acquisition system completed the setup. Setup is shown in Figure 6.



**Figure 1:** Fractionation test setup

### 4. EXPERIMENTAL PROCEDURE

The 1 liter stainless steel cylinder was filled at the desired fill density per the test requirement with the worst case formulation (WCF) blend and conditioned at the test temperature overnight, Figure 1. The cylinder is fitted with a top and bottom valve for vapor and liquid sampling. This cylinder is then placed in a stainless-steel cooling jacket which is kept cold by constant circulation of coolant from the chiller through the hoses to the circulating jacket to maintain steady temperature measured in the cylinder by a type K thermocouple calibrated to be  $\pm 0.5$  °C.

A “T” fitting is attached above the vapor exit valve allowing the pressure to be measured by a calibrated digital pressure gauge ( $\pm 1$  kPa). The vapor is “leaked” through a flow controller (laminar flow principal) which is calibrated

to determine the flow rate (ml/min) at  $\pm 2\%$  of indicated flow. The flow rate is maintained at 2% per hour of initial cylinder mass.

To determine the vapor composition, tubing is connected to the exit of the flowmeter and routed through a glass sampling flask at hourly intervals, then tested via gas chromatography.

To determine the liquid composition, a block and bleed valve is fitted to the bottom of the cylinder to yield a standardised small amount of liquid sample. Samples are taken at intervals of every fifth hour (5 hr \* 2% mass loss per hour = ~10% cylinder mass interval) so the influence of the liquid draw on the cylinder mass is minimized. The samples are tested via gas chromatography.

A GC with thermal conductivity detector (TCD) and a 22 ft long Carbograph 1% AT 1000 column with helium as a carrier gas were used to determine the concentration of the gases at different fractionation levels. The oven temperature was kept constant at 130°C. TCD detector was set at 200°C. A vapor sample was taken directly from a vapor hose; the liquid sample from the liquid line was flushed into pre-evacuated small 50 mL cylinder while monitoring the pressure not to exceed 1000 mmHg. 0.5 mL of vaporized liquid was then injected into GC using syringe with a shut off valve. Two calibration mixtures were used to determine the composition of the samples.

## 5. RESULTS AND DISCUSSIONS

### 3.1 Blend 1: R-473A

Fractionation analysis was carried out on the refrigerant blend R-473A as per ASHRAE Standard 34-2019. The analysis included storage leaks at 90% of maximum fill, equipment leaks at 15% of maximum fill and charge/recharge through five leakage events of 20% of each refrigerant charge. Since R-23, R-744 and R-125 are all qualified fire suppressants, the only component of flammable concern is R-1132a, so investigations are focused in determining conditions where the composition of this component is maximized in either the liquid or vapor phase.

To determine the WCF of the blend, the composition of R-1132a (the only flammable component in the blend) was set to its maximum value while R-23 and R-125 (fire suppressants) are set to their lowest values. R-744 is more of an oxygen displacer than fire suppressant so its composition was allowed to float in the analysis. The determined WCF composition is listed in Table 1.

An experimental fractionation study of a vapor leak from a cylinder initially filled to 90% of maximum fill at the temperature found to give the WCF for this blend which was -40°C. The maximum fill was calculated by reference to the estimated liquid density at a temperature of 6.2°C which was the fill temperature calculated from the equation (1) below ANSI/ASHRAE standard (note: we identified that the current equation in ASHRAE 34 is incorrect while doing this assessment, a suggestion has been submitted to the committee); leaks under storage/shipping conditions

$$T_{\text{fill}} = T_b + 0.8*(T_c - T_b) \quad (1)$$

Where  $T_{\text{fill}}$  is the 100% liquid fill temperature to be used in the WCF calculations,  $T_b$  is the bubble point temperature at atmospheric pressure (101.3 kPa), and  $T_c$  is the fluid/blend critical point temperature.

As R-473A has a critical temperature (29.7 °C) below the conditions required for testing of fluids whose critical temperature is lower than 130°F (54.4°C), the corresponding fill density used was 743 kg/m<sup>3</sup> giving an initial vapor quality of 0.304 for use in REFLEAK<sup>ii</sup> simulations which is a software package that performs various leakage scenarios and provide conclusive data of fluid interactions and behaviors during fractionation). The results of this fractionation study are presented in Figures 1-2 of this section and in Table 1.

The highest R-1132a content was found to be generated in the vapor phase partway through a vapor leak from a cylinder initially filled to 90% of the maximum fill with the WCF composition, at a temperature of -40°C. This composition was modelled to be a quaternary mixture of the composition listed in Table 1.

**Table 1:** WCF and WCFF compositions for use in fractionation and flammability study

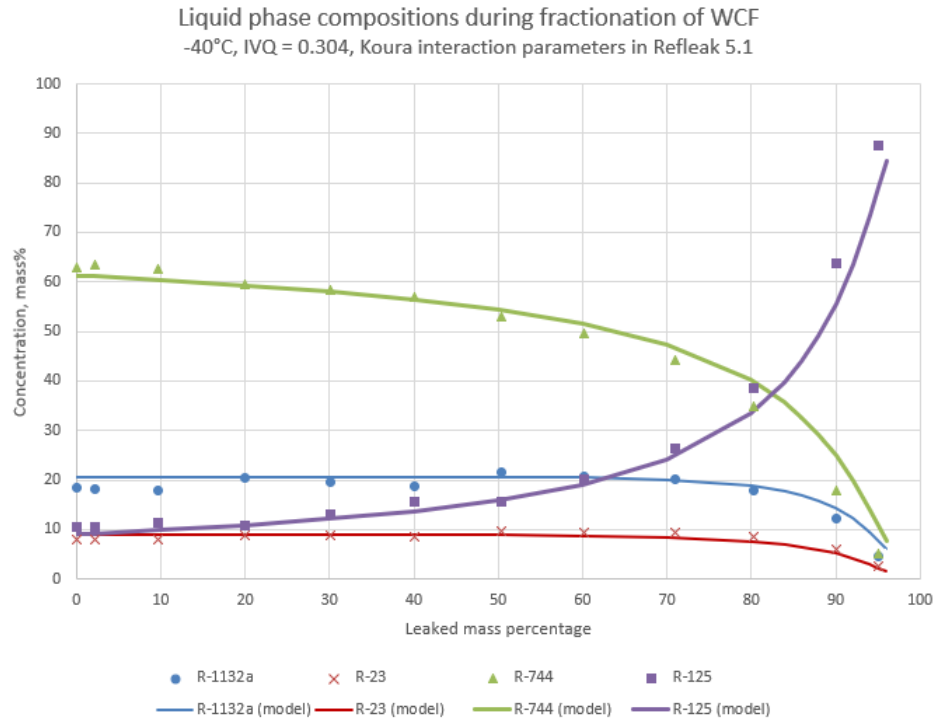
Component	Nominal %mass	WCF %mass	WCFF %mass
R-1132a	20.0 (+0.5/-1.0)%	20.5%	23.1%
R-23	10.0 ( $\pm$ 1.0)%	9.0%	10.8%
R-744	60.0 ( $\pm$ 2.0)%	61.5%	48.3%
R-125	10.0 ( $\pm$ 1.0)%	9.0%	17.8%

The experimental fractionation study was conducted using the conditions that gave rise to the WCFF and the resulting data are reported in Table 2. The measured composition trajectories matched the modelled composition trajectories very closely with the model predicting a slightly lower maximum in the concentration of R-1132a at the WCFF position. The WCFF was selected conservatively as that found by experiment to give the maximum concentration of R-1132a as a mass percentage.

**Table 2:** Experimental Fractionation Study Compositions at 90% max fill, -40°C using WCF as initial fill

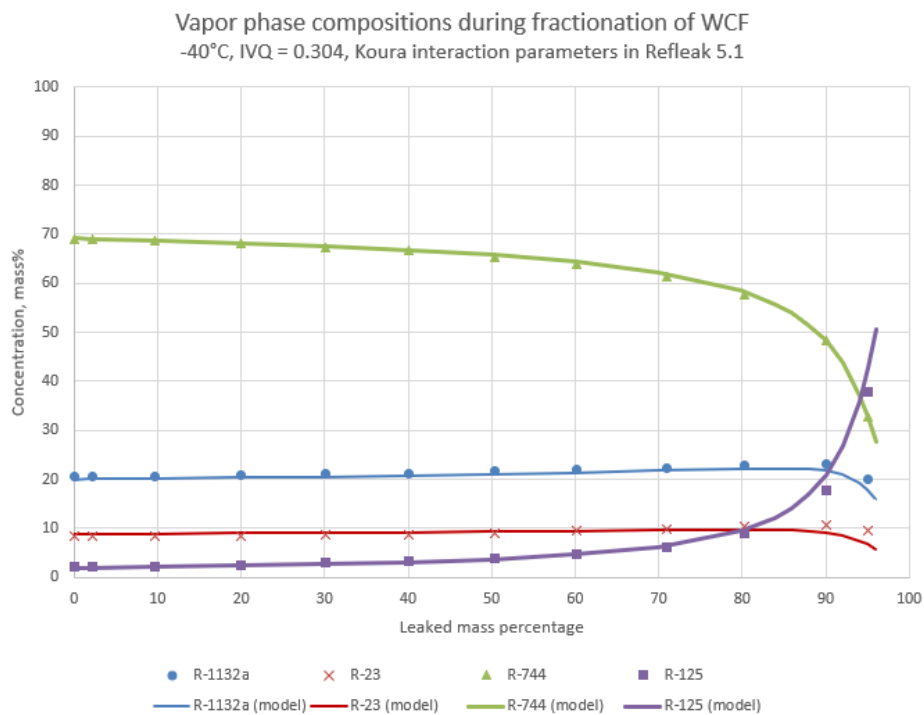
%Loss	R-1132a	R-23	R-744	R-125	R-1132a	R-23	R-744	R-125
	Liquid Mass%	Liquid Mass%	Liquid Mass%	Liquid Mass%	Vapor Mass%	Vapor Mass%	Vapor Mass%	Vapor Mass%
0.00	18.4	8.1	63.0	10.4	20.5	8.3	68.9	2.2
2.21	18.1	8.1	63.4	10.4	20.5	8.3	68.9	2.2
9.64	17.9	8.1	62.7	11.3	20.7	8.4	68.6	2.3
20.00	20.4	9.0	59.6	11.0	20.9	8.5	68.0	2.6
30.06	19.6	8.8	58.5	13.1	21.1	8.7	67.3	2.9
40.07	18.8	8.6	57.0	15.6	21.2	8.8	66.8	3.3
50.33	21.5	9.6	53.1	15.8	21.6	9.1	65.4	3.9
60.16	20.7	9.5	49.7	20.1	22.0	9.4	63.8	4.8
70.97	20.1	9.3	44.3	26.3	22.4	9.8	61.5	6.3
80.20	18.0	8.6	34.9	38.5	22.9	10.3	57.7	9.0
<b>90.09</b>	<b>12.2</b>	<b>6.1</b>	<b>17.8</b>	<b>63.9</b>	<b>23.1</b>	<b>10.8</b>	<b>48.3</b>	<b>17.9</b>
95.11	4.7	2.5	5.1	87.6	19.9	9.6	32.8	37.7

The experimentally derived WCFF composition is highlighted in bold face in Table 2; it was that in the vapor after 90% mass loss. This composition when tested by the standard test method for concentration limits of flammability of vapors (vapors and gases) (ASTM E681-09(2015))<sup>iii</sup> was found to be non-flammable. (Grundy, et al. 2022)<sup>iv</sup>



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

Solid lines show modelled results; points show experimentally determined compositions.



**Figure 2:** Comparison of Modelled Vapor Compositions vs Experimental Fractionation

Solid lines show modelled results; points show experimentally determined compositions.

The following fractionation scenarios were then modelled using REFLEAK 5.1 starting from the selected WCF:

- (a) Leakage from storage: 90% of maximum fill in temperature range -40 to +54°C
- (b) Leakage from equipment: 15% of maximum fill in temperature range -40 to +60°C
- (c) Leak and recharge: starting from 15% maximum fill, leak 20% charge by vapor at 23°C then refill with original composition

The selected density for maximum fill was 826 kg/m<sup>3</sup> giving 90% of maximum fill as a density of 743 kg/m<sup>3</sup> and 15% of maximum fill as a density of 124 kg/m<sup>3</sup>. It was noted that at temperatures above 20°C the liquid density of the WCF composition would be lower than 743kg/m<sup>3</sup>, so that in evaluation of fractionation behavior at temperatures above 20°C for the “90% fill” scenario the initial vapor quality for the leak was set to a near-zero value of 0.001.

It was likewise noted that the saturated vapor density of the WCF would be greater than 124 kg/m<sup>3</sup> at temperatures above 7.5°C, so that there would be no possibility of fractionation for the 15% fill scenario at temperatures above 7.5°C (because the leak would be from a single vapor-phase system).

The maximum concentration of R-1132a arises in the vapor phase for a 90% fill and a leakage temperature of -40°C with a slow vapor leak. R-473A has been classified as an A1 (non-toxic, non-flammable) refrigerant by ASHRAE Standard 34.

### 3.2 Blend 2 : LFR3

The “LFR3” blend (R-1132a/R-744/R-32 with composition 10/69/21%) is to be submitted for ISO817<sup>v</sup> for an A1/A2L split classification. The WCF is the intended composition of the refrigerant that has been modified to maximize the flammable components within the chosen blend tolerances namely (Table3). This will be WCF both for flammable limit and for burning velocity. Both the nominal and WCF formulations are non-flammable at 23°C and 60°C.

Filling densities of 750, 250 and 125 kg/m<sup>3</sup> and leakage temperatures of -40°C, 0° C, 20°C, and 25°C were studied. These correspond to the 90% and 15% fill limits specified by ASHRAE standard 34.

The conditions giving rise to the WCF have been found by running a range of REFLEAK v5.1 simulations using internal interaction parameters set and fluid model for R-1132a. The conditions which give rise to the WCF are vapor leakage from a 90% filled cylinder at a temperature of -40°C. The WCF is predicted to occur in the liquid phase after 95% mass loss, and to be a binary blend of 98.7% R-32, 1.3% R-744. It is important to note that this leak scenario represents a cylinder leak and not a system leak.

**Table 3:** WCF and WCFF compositions for use in fractionation and flammability study

Component	Nominal %mass	WCF %mass	WCFF %mass
R-1132a	10.0 (+1.0)%	11 %	0%
R-32	21.0 (±1.0)%	22 %	98.7 %
R-744	69.0 (±2.0)%	67 %	1.3 %

The WCFF was conducted at the conditions predicted to give rise to the stated WCFF stated. The cylinder fill density was 750 gram/liter and the test was conducted at -40°C with a variation of ±1K. Vapor leakage rate was controlled at 2% per hour by a mass flow controller. Vapor and liquid phases were analyzed using GC analysis at 0%, 2% and then 10% intervals to 90% mass loss. This experimental data was used to validate the REFLEAK model conclusions. The results are summarized in (Table 4).

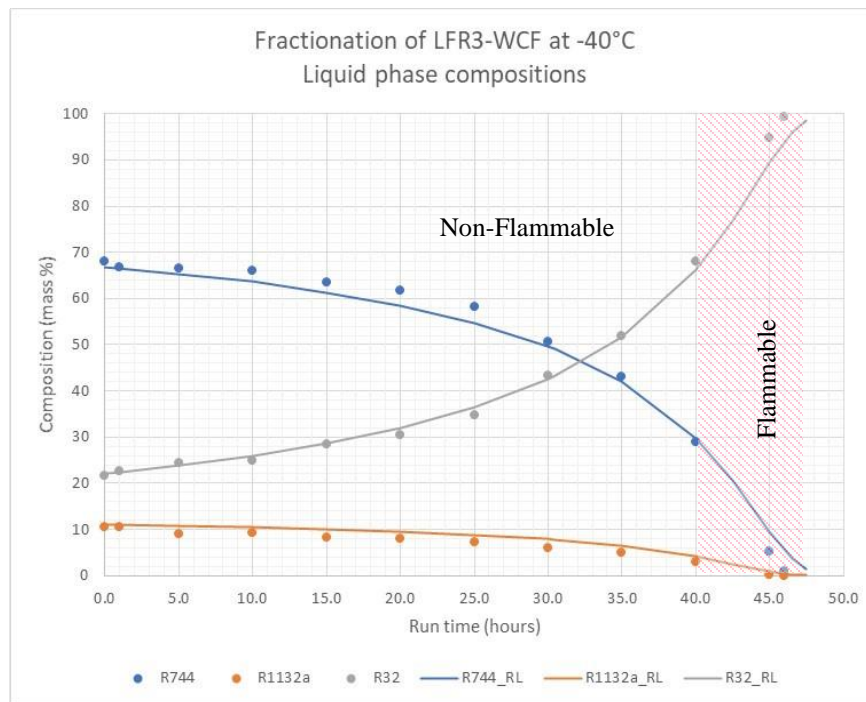
**Table 4:** Experimental fractionation data for WCF at -40°C

<b>Run time (hrs)</b>	<b>Pressure (bar)</b>	<b>R-1132a Liquid Mass%</b>	<b>R-32 Liquid Mass%</b>	<b>R-744 Liquid Mass%</b>	<b>R-1132a Vapor Mass%</b>	<b>R-32 Vapor Mass%</b>	<b>R-744 Vapor Mass%</b>
0.0	8.69	10.52	21.50	67.98	11.74	5.08	83.18
1.0	8.16	10.42	21.50	66.89	12.19	5.31	82.50
5.0	7.90	9.11	24.34	66.55	11.91	5.49	82.60
10.0	7.65	9.20	24.88	65.91	11.39	5.76	82.85
15.0	7.41	8.18	28.45	63.37	10.97	6.17	82.87
20.0	7.21	7.88	30.49	61.63	11.22	7.22	81.56
25.0	6.80	7.25	34.68	58.08	10.87	8.39	80.75
30.0	6.47	6.02	43.26	50.72	10.06	10.49	78.76
35.0	5.67	4.92	51.91	43.17	10.06	14.31	75.63
<b>40.0</b>	<b>4.22</b>	<b>2.91</b>	<b>68.13</b>	<b>28.97</b>	<b>8.36</b>	<b>23.69</b>	<b>67.95</b>
45.0	1.92	0.10	94.73	5.17	2.89	53.43	43.68
46.0	1.23	0.00	99.21	0.81	0.72	76.82	22.45

The leakage was modelled in REFLEAK 5.1 using our interaction parameters and fluid model for R-1132a. The comparison is shown in Figures 3 and 4 for the vapor and liquid phases. While there is some deviation between measured and modelled concentration of R-744 the trends are correctly predicted. The end-point liquid composition at 95% mass loss has the highest concentration of flammable fluorocarbon R-32 and is the WCF. It is also the point when there isn't sufficient material in the cylinder to leak (the cylinder is at atmospheric pressure in this condition).

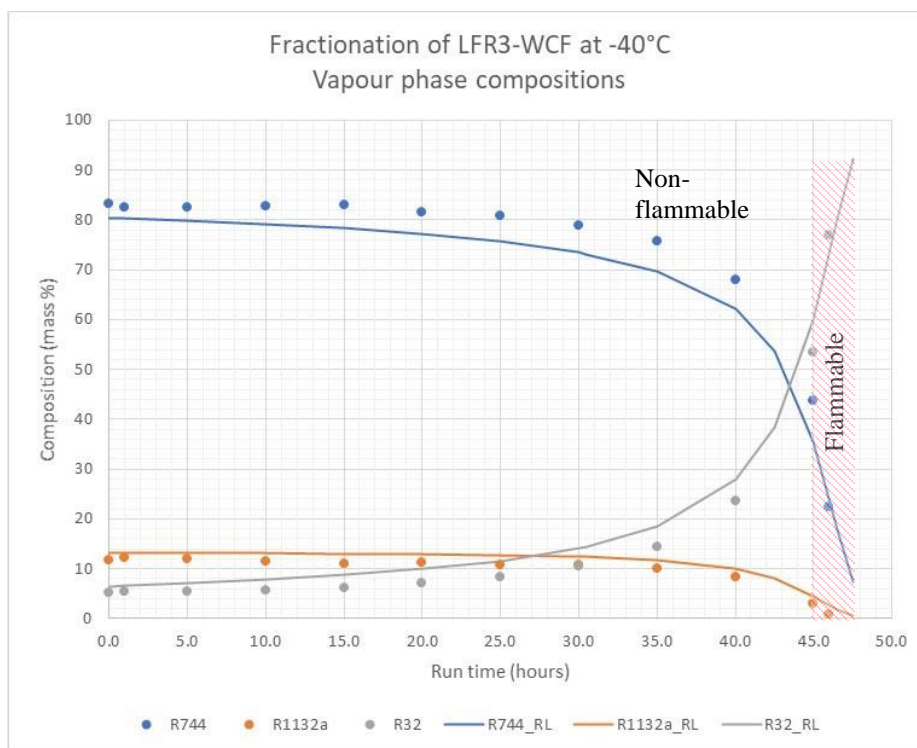
ASTM E681 Flammability testing was conducted on the different compositions found in the leak profile (Grundy, et al. 2022). During this testing, it was found that LFR3 became flammable when the R-32 content rose above 55% and the CO<sub>2</sub> was unable to continue suppressing flame formation (CO<sub>2</sub> and R-1132a are 40% and 5.5% respectively). This is promising as the blend has now significantly shifted from the nominal concentration and equipment performance has shifted to a less than desirable level prompting service. It also allows us to investigate further how to design equipment for possible non-flammable operation.





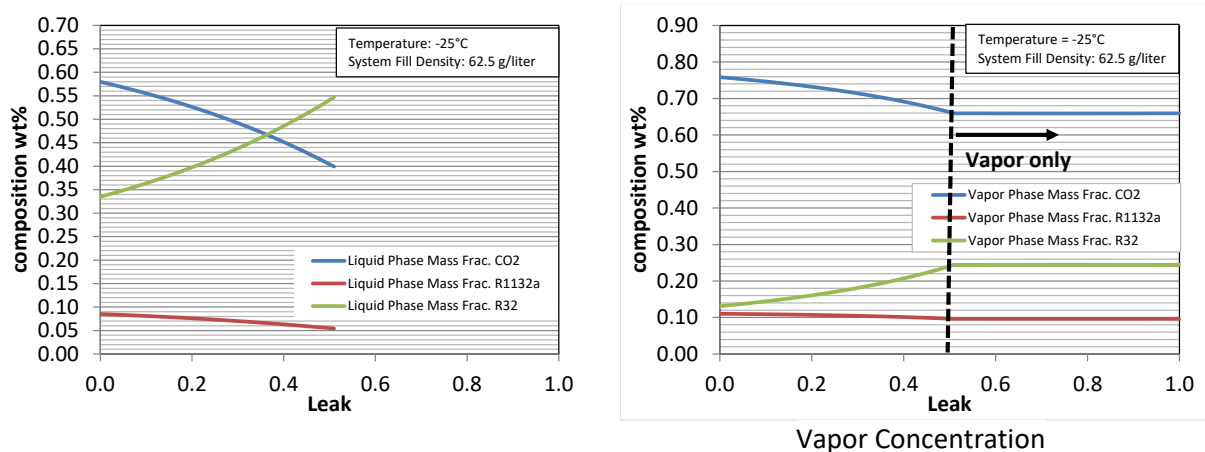
**Figure 3:** Comparison of Modelled Liquid Compositions vs Experimental Fractionation

Solid lines show modelled results; points show experimentally determined compositions.



**Figure 4:** Comparison of Modelled Vapor Compositions vs Experimental Fractionation

As seen in Figure 5, it is possible to select alternative equipment charge amounts for low temperature operation where equipment will never experience a flammable concentration. For instance, we submit that at  $-25^{\circ}\text{C}$  ( $-4^{\circ}\text{F}$ ) temperature is the lowest that the majority of heat pump equipment will ever experience for a time, long enough to leak slow enough to fractionation in this hypothetical manner (time period of multiple days, continuously). *If a charge density of 62.3 grams/liter (system charge pressure of 26 barg) is adopted through the strategic use of a suction fadeout tank and microchannel heat exchangers, then even in the worst case, the material in the system remains non-flammable.* This design principal is commonplace in most low temperature refrigeration equipment today where the charge nameplate lists a charge pressure rather than a system charge weight – it is inferred that the temperature is room temperature unless specified.



**Figure 5:** Modelled Liquid and Vapor Compositions of LFR3 for a slow vapor leak at  $-25^{\circ}\text{C}$

R-473A has successfully been submitted to ASHRAE and classified as an A1 refrigerant to be used as a lower GWP option to R-23 or R-508B.

When initially submitted, LFR3 was not granted the split A1/A2L classification. We believe that the data shows that through the selection of an appropriate charge density, it is possible to charge a system so that it does not become flammable regardless of the leak scenario.

## 6. CONCLUSIONS

This paper presents results for obtaining non-flammable classification for R-473A as per ASHRAE Standard 34. The experimental results fit very close to the modelled composition for R-473A, which verifies the interaction parameters in our REFPROP<sup>vi</sup> model. After testing the WCFF in a separate ASTM E681 apparatus the conclusion is that for all leakage scenarios, R-473A is non-flammable.

For LFR3, the leakage path for vapor and liquid correlates to our model calculations. The WCF established here was tested by Grundy via ASTM E681 and was found to be non-flammable. We believe the  $-40^{\circ}\text{C}$  condition is too stringent for HP equipment as only a very tiny number of units will ever experience a condition that cold long enough to represent a slow vapor leak scenario. We submit that  $-25^{\circ}\text{C}$  may be a better control point with regards to system safety and vapor fractionation. A study was conducted on how a system may maintain non-flammable status in worst case leaks and with proper selection of charge amount we found that it is possible for LFR3 with a charge density less than  $62.5\text{ kg/m}^3$  ( $62.5\text{ g/liter}$ ). Our position is that LFR3 be granted a ASHRAE Standard 34 and ISO 817 dual classification of A1/A2L to signify that this material can be used as a non-flammable, but there are special issues that need to be addressed through system engineering or there is the possibility of a flammable material where additional precautions need to be taken.

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- 
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