HFO-1234yf

A Low GWP Refrigerant For MAC

Honeywell / DuPont Joint Collaboration

Mark Spatz

Honeywell

Barbara Minor

DuPont

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Background

- DuPont And Honeywell Have Identified HFO-1234yf ($CF_3CF{=}CH_2$) As The Preferred Low GWP Refrigerant Which Offers The Best Balance Of Properties And Performance
- Other Industry Options Have Certain Limitations
  - CO_2 : complexity, energy efficiency and requires mitigation
  - 152a / secondary loop: performance, size and weight

Honeywell and DuPont are focused on HFO-1234yf

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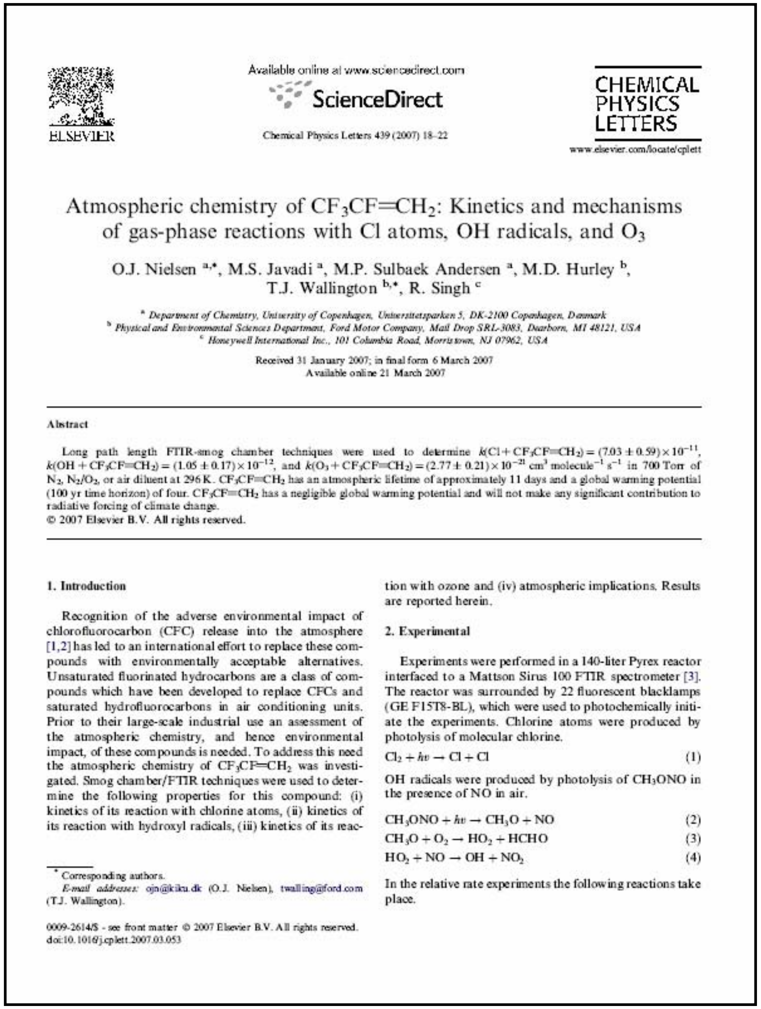
HFO-1234yf Summary

Honeywell

- **Excellent environmental properties**
  - Very low GWP of 4, Zero ODP, Favorable LCCP
  - Atmospheric chemistry determined and published
- **Low toxicity, similar to R-134a**
  - Low acute and chronic toxicity
  - Significant testing completed
- **System performance very similar to R-134a**
  - Excellent COP and Capacity, no glide
    - From both internal tests and OEM tests
  - Thermally stable and compatible with R-134a components
  - Potential for direct substitution of R-134a
- **Mild flammability (manageable)**
  - Flammability properties significantly better than 152a; (MIE, burning velocity, etc)
  - Potential for “A2L” ISO 817 classification versus “A2” for 152a based on AIST data
  - Potential to use in a direct expansion A/C system - better performance, lower weight, smaller size than a secondary loop system

Excellent Environmental Properties

- **ODP = 0**
- **100 Year GWP = 4** (GWP$_{134a}$ = 1300)
  - Measurements completed & published:
    "Atmospheric Chemistry of $CF_3CF=CH_2$"
    Chemical Physics Letters 439 (2007) pp 18-22
- **Atmospheric lifetime = 11 days**
- **Atmospheric chemistry measured**
  - Atmospheric breakdown products are the same as for 134a
  - No high GWP breakdown products (e.g. **NO** HFC-23 breakdown product)
  - Results published in 2008
- **Good LCCP**



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Atmospheric chemistry of $CF_3CF{=}CH_2$: Kinetics and mechanisms of gas-phase reactions with Cl atoms, OH radicals, and O_3

O.J. Nielsen [a,*], M.S. Javadi [a], M.P. Sulbaek Andersen [a], M.D. Hurley [b], T.J. Wallington [b,*], R. Singh [c]

[a] Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark
[b] Physical and Environmental Sciences Department, Ford Motor Company, Mail Drop SRL-3083, Dearborn, MI 48121, USA
[c] Honeywell International Inc., 101 Columbia Road, Morristown, NJ 07962, USA

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Abstract

Long path length FTIR-smog chamber techniques were used to determine $k(Cl + CF_3CF{=}CH_2) = (7.03 \pm 0.59) \times 10^{-11}$, $k(OH + CF_3CF{=}CH_2) = (1.05 \pm 0.17) \times 10^{-12}$, and $k(O_3 + CF_3CF{=}CH_2) = (2.77 \pm 0.21) \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} in 700 Torr of N_2, N_2/O_2, or air diluent at 296 K. $CF_3CF{=}CH_2$ has an atmospheric lifetime of approximately 11 days and a global warming potential (100 yr time horizon) of four. $CF_3CF{=}CH_2$ has a negligible global warming potential and will not make any significant contribution to radiative forcing of climate change.

1. Introduction

Recognition of the adverse environmental impact of chlorofluorocarbon (CFC) release into the atmosphere [1,2] has led to an international effort to replace these compounds with environmentally acceptable alternatives. Unsaturated fluorinated hydrocarbons are a class of compounds which have been developed to replace CFCs and saturated hydrofluorocarbons in air conditioning units. Prior to their large-scale industrial use an assessment of the atmospheric chemistry, and hence environmental impact, of these compounds is needed. To address this need the atmospheric chemistry of $CF_3CF{=}CH_2$ was investigated. Smog chamber/FTIR techniques were used to determine the following properties for this compound: (i) kinetics of its reaction with chlorine atoms, (ii) kinetics of its reaction with hydroxyl radicals, (iii) kinetics of its reaction with ozone and (iv) atmospheric implications. Results are reported herein.

2. Experimental

Experiments were performed in a 140-liter Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer [3]. The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL), which were used to photochemically initiate the experiments. Chlorine atoms were produced by photolysis of molecular chlorine.

$$Cl_2 + h\nu \rightarrow Cl + Cl \quad (1)$$

OH radicals were produced by photolysis of CH_3ONO in the presence of NO in air.

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \quad (2)$$
$$CH_3O + O_2 \rightarrow HO_2 + HCHO \quad (3)$$
$$HO_2 + NO \rightarrow OH + NO_2 \quad (4)$$

In the relative rate experiments the following reactions take place.

* Corresponding authors.
E-mail addresses: ojn@kiku.dk (O.J. Nielsen), twalling@ford.com (T.J. Wallington).

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Significant Toxicity Information Available

Test	HFO-1234yf	134a	
• Acute Lethality	No deaths 400,000 ppm	No deaths 359,700 ppm	✓
• Cardiac sensitization	NOEL > 120,000 ppm	NOEL 50,000 ppm LOEL 75,000 ppm	✓
• 13 week inhalation	NOEL 50,000 ppm	NOEL 50,000 ppm	✓
• Developmental (Rat)	NOAEL 50,000 ppm	NOAEL 50,000 ppm	✓
• Genetic Toxicity	Not Mutagenic	Not Mutagenic	✓
• 13 week genomic (carcinogenicity)	Not active (50,000 ppm)	Baseline (50,000 ppm)	✓
• Environmental Tox	NOEL > 100 mg/L (Pass)	NOEL > 100 mg/L (Pass)	✓

HFO-1234yf Has Low Toxicity

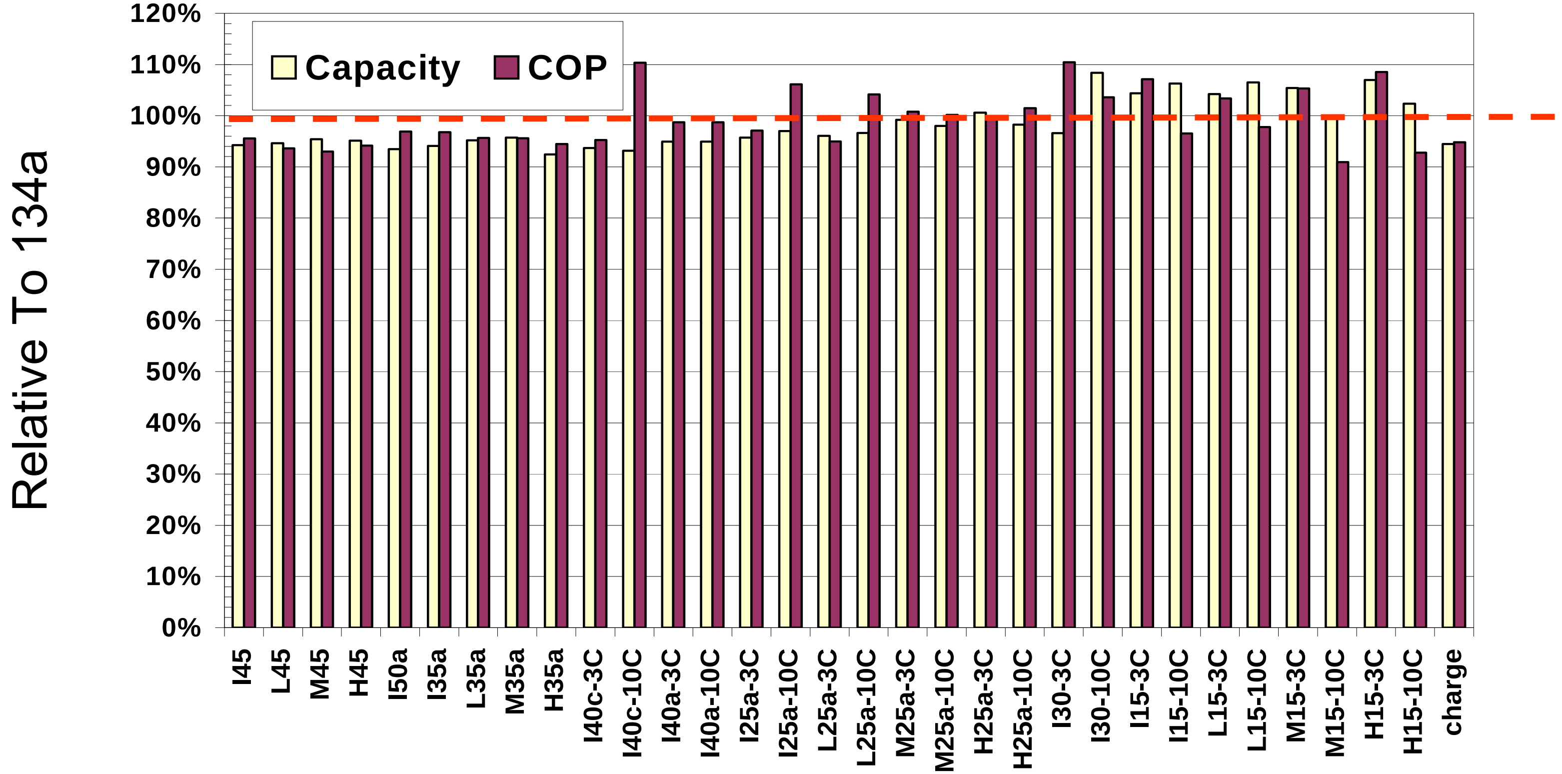
ATEL Calculation

- ATEL (Acute Toxicity Exposure Limit) is a value used by standards organizations (e.g. ASHRAE 34) to reduce the risks of acute toxicity hazards in normally occupied spaces.
- It is calculated from the acute toxicity data for a given refrigerant and provides an estimate of the maximum exposure limit for a short time period (e.g. 30 minutes)

Refrigerant	ATEL (ppm)
R-12	18,000
R-134a	50,000
R-152a	50,000
CO_2	40,000
HFO-1234yf	101,000

HFO-1234yf Has a Favorable ATEL Value

System Bench Test Results



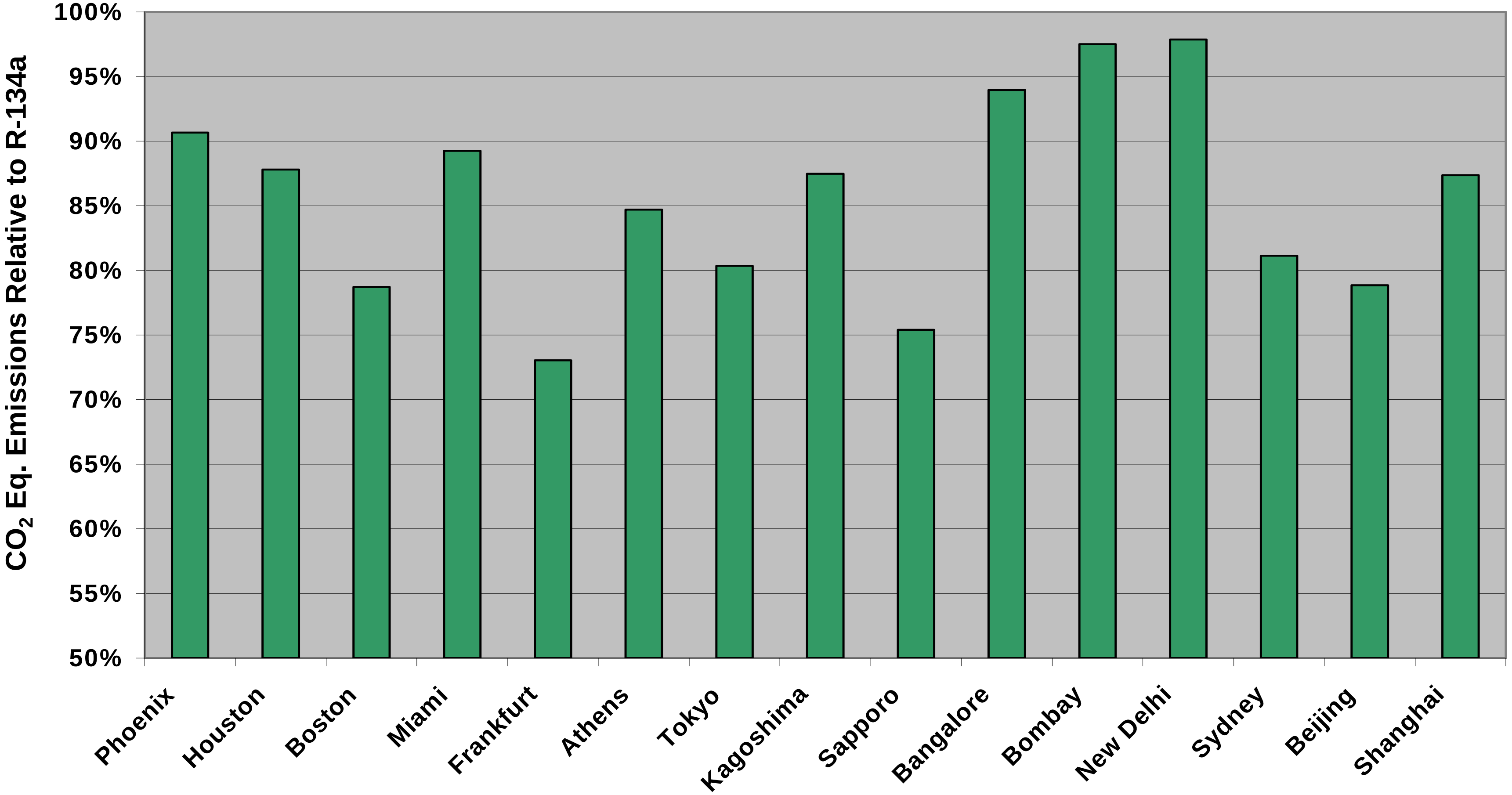
- No changes were made to system including TXV; Industry standard test conditions
- Both Capacity and COP are generally within 5% of 134a performance.
  - This was recently confirmed at two outside labs.
- Lower compression ratio, low discharge temperature (12°C lower at peak conditions)
- Further improvements likely with minor system optimization, for example:
  - Lower ΔP suction line and / or TXV optimization to maintain a more optimum superheat.

HFO-1234yf performance is comparable to 134a; further improvement possible with minor optimization

HW/DuPont Data

Preliminary LCCP Analysis

GM Model Using Bench Test Performance Results Relative to R-134a



Average 15% Better LCCP Values; Up to 27% in Europe

JAMA and FIAT Obtained Similar Results

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Compressor Test Results

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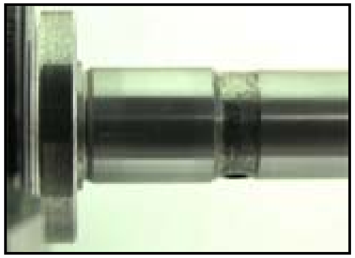
Summary

- Low Charge, High Pressure, Heated Compressor Environment, 2000 RPM, 400 hour test
- No change detected in either refrigerant or lubricant chemistry
  - Initial and final oil sample TAN < 0.1
  - Refrigerant purity remained at 99.8% with no change in trace impurities.
- Wear is same as in a 134a system
- Polishing is seen on the Front and Rear Shaft Bearings & Rear Thrust Bearing
- Swash-plate polymer coating is intact and shows only minor wear
- Results confirmed in compressor tests by Sanden

Pre-Test | Post-Test

Front Shaft Bearing



Rear Shaft Bearing

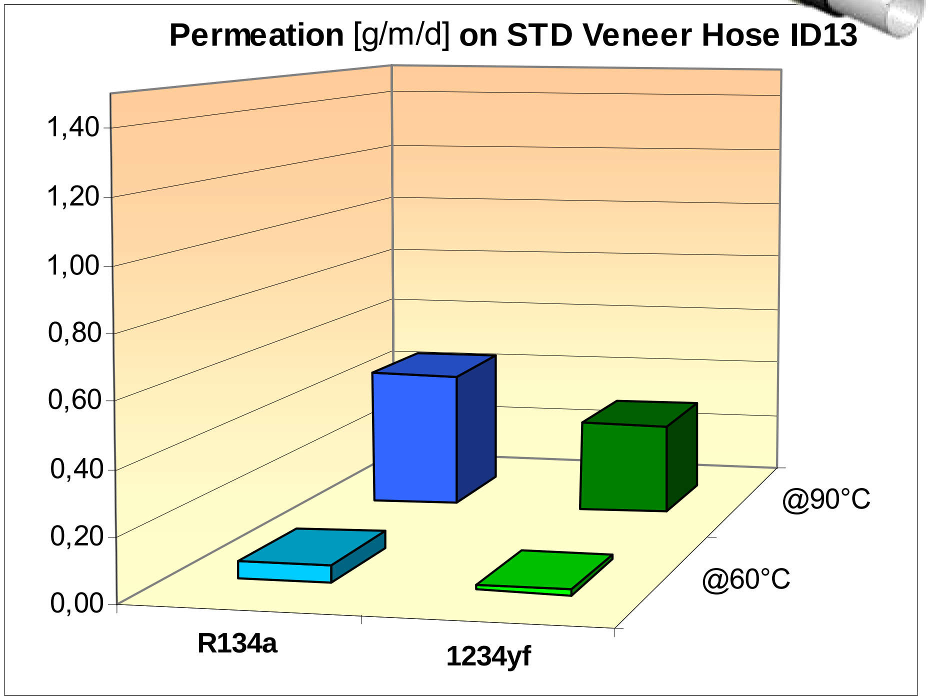
Rear Thrust Bearing

Swash Plate

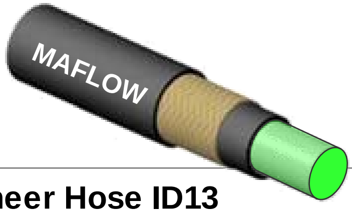
Compressor Wear Same as 134a

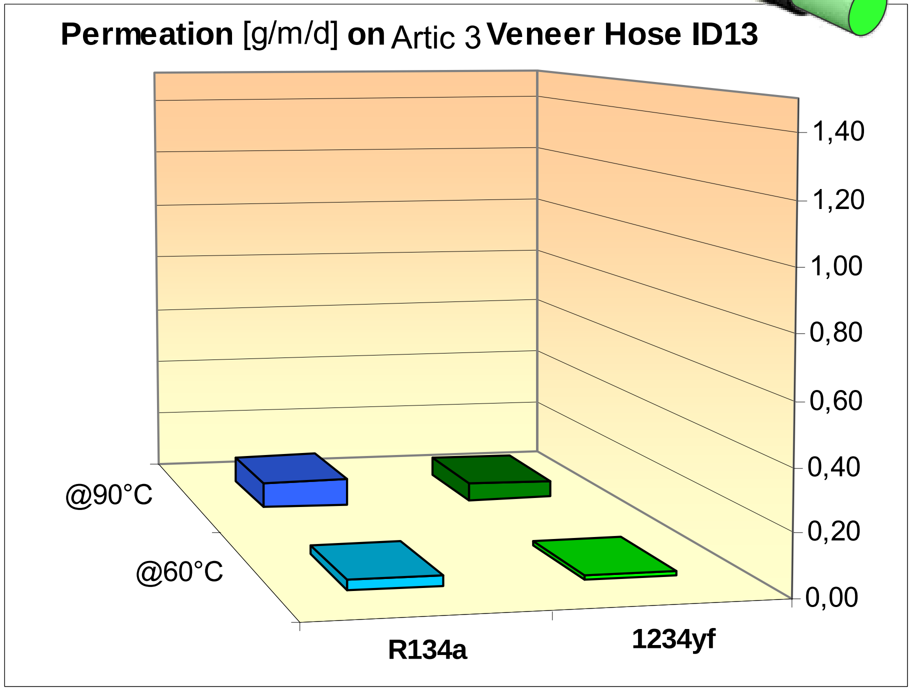
Permeation HFO-1234yf vs R-134a

Standard Veneer Hose



ULEV Veneer Hose





Results

HFO-1234yf shows lower permeability values toward Veneer hoses compared to R134a.

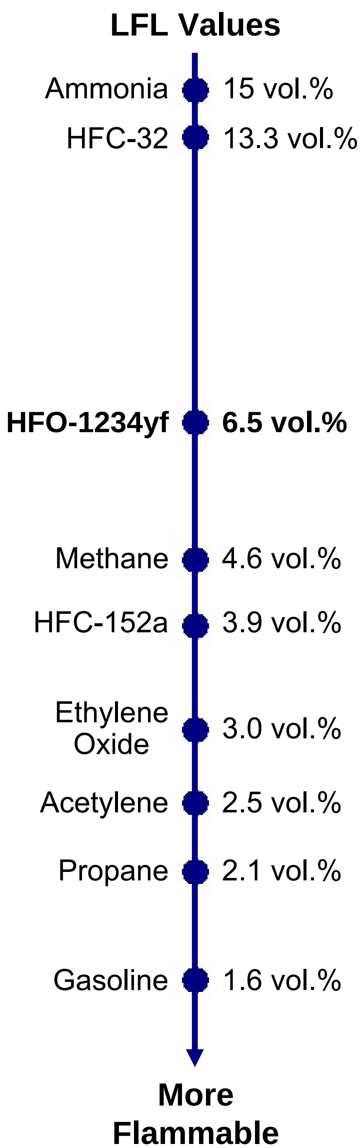
Remarks

With the same gas concentration (0.6g/cm³) the inner pressure with HFO-1234yf is lower (e.g: at 90°C was -20%)

Refrigerant Flammability Tests

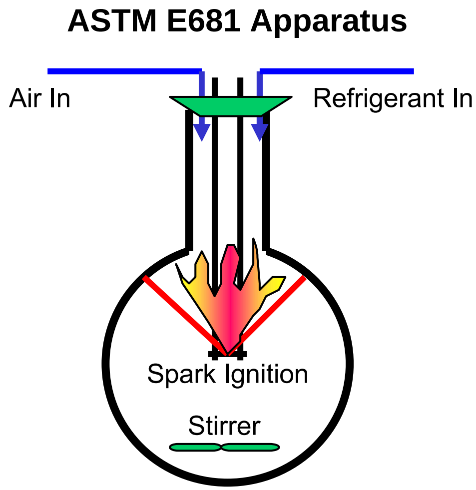
- Is it flammable? If yes, Flame Limits will exist.
  - LFL – lower flammability limit
  - UFL – upper flammability limit
- What is the probability of an ignition source being present of sufficient energy to cause an ignition?
  - Autoignition temperature
  - Minimum ignition energy (MIE)
- What is the impact (damage potential) if an ignition occurs?
  - Heat of combustion
  - Burning velocity

HFO-1234yf Flame Limits



- HFO-1234yf flame limits measured using ASTM E681-04 T= 21°C : 6.5 vol.% to 12.3 vol.%

- **Low LFL value → more flammable**
- Wider UFL – LFL → more flammable



- ASTM E-681 in US
  - 2004 version cited by ASHRAE (12 liter flask, spark ignition)
  - Flame must reach the wall and exhibit > 90 degree angle
  - 1985 version cited by SAE (5 liter flask, match ignition)
- A11 in EU
  - 5 cm x 30 cm Vertical tube
  - Spark ignition
  - Flame travels up the tube

HFO-1234yf Is Less Flammable Than 152a

Burning Velocity

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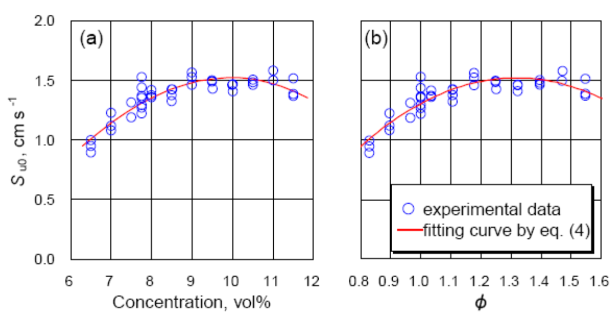
Burning velocity as a function of
(a) concentration and (b) equivalence ratio



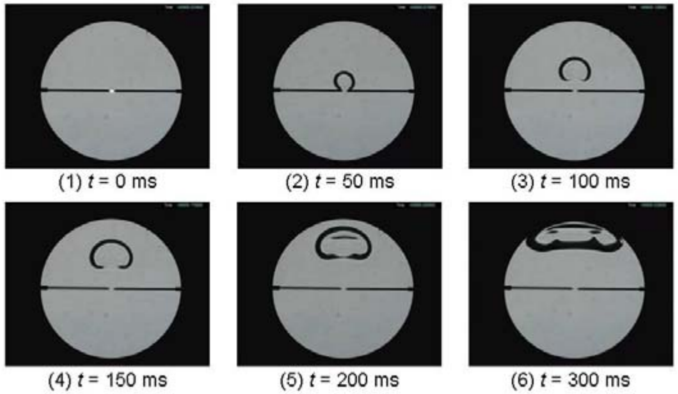
By fitting all the data to a paraboric function (4), maximum S_{u0} was obtained as 1.52 cm s^{-1} at ϕ =1.32. Therefore, the maximum S_{u0} is 1.5 cm s^{-1} at ca. 10 vol%.

$$S_{u0} = S_{u0,max} + s_1 (\phi - \phi_{max})^2 \quad (4)$$

$$= 1.52 - 2.13 (\phi - 1.32)^2$$

Appendix **Example of schlieren photography method** AIST

1234yf, 7.75 % (ϕ = 1), P_0 = 760 Torr, T_0 =291.45 K



Flame radii in the horizontal direction (r_f) were measured to minimize the effect of buoyancy. In this case I used the data from t = 50 to 150 ms, during which the flame front was not affected by any objects.

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Burning Velocity Measurements

- Measurements performed in 3 liter spherical apparatus
- Experimental result for HFO-1234yf: 1.5 cm s^{-1}
- ISO 817 Flammability Classification is 2L (lowest flammable class classification)

	Propane	152a	NH_3	32	1234yf
BV, cm s^{-1}	46	23	7.2	6.7	**1.5***

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Minimum Ignition Energy

- 12-liter glass sphere used in ASTM E681 flammability limit tests was modified for MIE testing in order to eliminate potential wall quenching effects seen in standard 1 liter vessel
- Materials Tested:
  - HFC-32 from 16-22% (v/v) in 1% increments at 30 and 100 mJ nominal
  - HFO-1234yf from 7.5-11% (v/v) in 0.5% increments up to 1000 mJ nominal
  - Ammonia at 22% (v/v) at 100 and 300 mJ nominal

Refrigerant	*No Ignition Occurred*	*Ignition Occurred*
HFC-32	30 +/- 12 mJ	100 +/- 30 mJ
Ammonia[1]	100 +/- 30 mJ	300 +/- 100 mJ
HFO-1234yf	5,000 +/- 350 mJ	10,000 +/- 350 mJ

HFO-1234yf Is Very Difficult To Ignite With Electrical Spark

HFO-1234yf Mild Flammability Properties

Flammability Properties

	LFL[a] (vol%)	UFL[a] (vol%)	Δ (vol%)	MIE (mJ)	BV[c] (cm/s)
Propane	2.2	10.0	7.8	0.25	46
R152a	3.9	16.9	13.0	0.38	23
R32	14.4	29.3	14.9	30-100[b]	6.7
Ammonia	15	28	13	100-300[b]	7.2
HFO-1234yf	6.5	12.3	5.8	>1,000[b]	1.5

[a]Flame limits measured at 21 C, ASTM 681-01
[b]Tests conducted in 12 litre flask to minimize wall quenching effects
[c]Burning Velocity ISO 817 (HFO-1234yf BV measured by AIST, Japan)

Flammability Index

	R	F	RF	RF2
HFO-1234yf	**0.97**	**0.27**	**3.6**	**0.6**
32	**1.31**	**0.33**	**4.6**	**2.3**
152a	**1.78**	**0.5**	**16.6**	**17.9**
Propane	**1.99**	**0.55**	**56.7**	**37.2**

$$R = \frac{Cst}{LFL}$$

$$F = 1 - \sqrt{\left(\frac{LFL}{UFL}\right)}$$

$$RF = \left[\sqrt{\left(\frac{UFL}{LFL}\right)} - 1\right] \times \frac{Q}{M}$$

$$RF2 = \left\{\left(\sqrt{(UFL \times LFL)} - LFL\right) / LFL\right\} \times Qst \times Su$$

Cst = *Stoichiometric composition in air, vol.%*

Q = *Heat of Combustion per one mole*

Qst = *Heat of Combustion per one mole of the Stoichiometric mixture, kJ/mol*

Su = *Burning speed in Meters/Second*

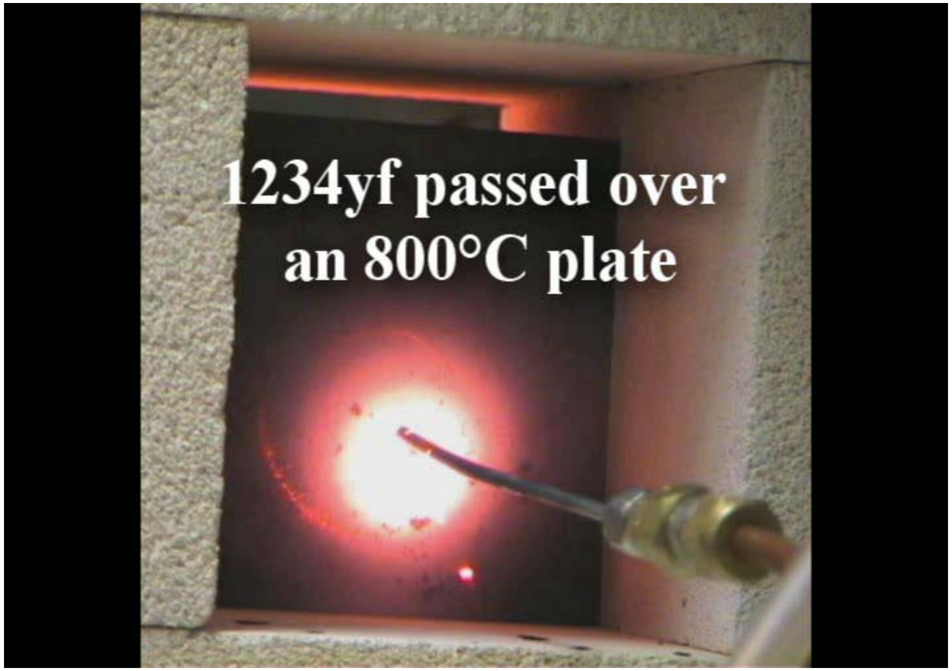
M = *Molecular weight*

Autoignition Temperature & Hot Surface Ignition

- **The autoignition temperature of HFO-1234yf was determined at Chilworth Technology in UK.**
  - **Uniformly heated 500 ml glass flask, observed in dark for 10 mins.**
  - **Autoignition temperature for HFO-1234yf determined to be 405ºC.**

- **Note that the air refrigerant mixture must be at this temperature for ignition to occur.**

- **Experiments were conducted to evaluate the ignition potential of hot surfaces (up to 800ºC) to cause ignition.**
  - **6 mm steel plate heated from behind with propane-oxygen torch**
  - **No ignition seen**



• HFO-1234yf vapor sprayed onto the plate
• Infrared Thermometer measured temperature.
  • Three "dots" seen are to aim the thermometer
• Occasional red circles are diffraction rings from the camera lens reflecting the red plate through the refractive index gradient (caused by hot air / cold refrigerant).

Summary of Hot Plate Tests

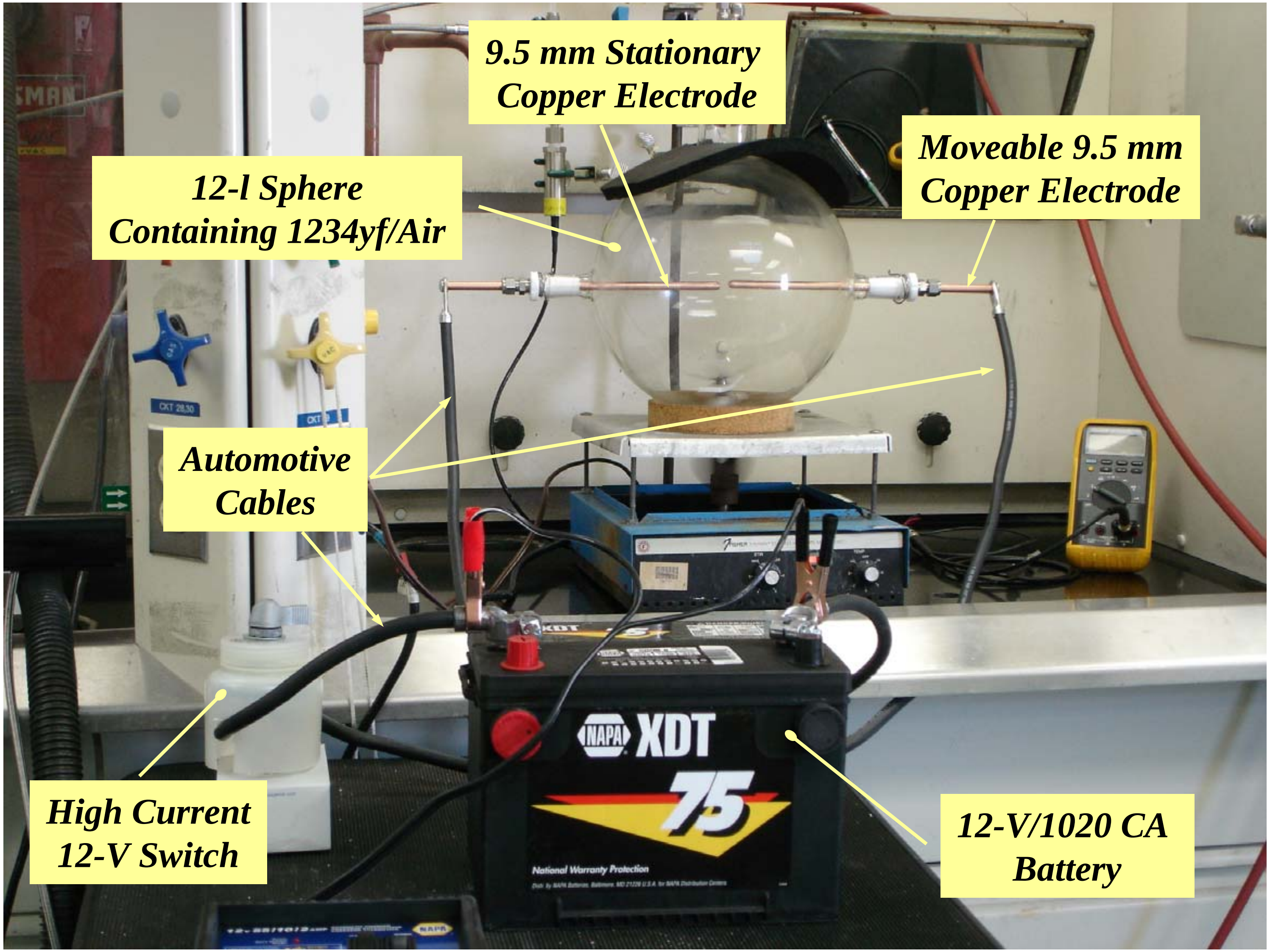
		Hot Manifold		
		550°C Faint Red	800°C Cherry Red	>900°C Orange
HFO-1234yf	Spray No oil	No ignition	No ignition	No ignition
	Premixed with air no oil	Not tested	No ignition	No ignition
	with PAG oil	No ignition	No ignition	Ignition
R-134a	Spray no oil	No ignition	No ignition	No ignition
	Premixed with air no oil	Not tested	No ignition	No ignition
	with PAG oil	No ignition	No ignition	Ignition

HFO-1234yf shows same flammability behavior as R-134a - Ignition due to presence of oil

HFO-1234yf Ignitability to Spark from 12-V Battery Short Circuit

- A potential ignition source for potentially flammable refrigerant/air leaks in passenger compartment of cars is a spark caused by a short circuit from a 12-V battery located under the seat
- The purpose of these tests is to determine whether such a spark is capable of igniting an ‘optimum’ concentration of HFC1234yf in air
- Follow procedures from ASTM E681 to prepare a well-blended refrigerant/air mixture of a known concentration in a sealed 12-l spherical flask; add moisture equivalent to 50% RH at 23^{o} C
- Create a short-circuit in the mixture by discharging a high-capacity 12-V automotive battery (1020 cranking amps) across 9.5 mm diameter copper electrodes located in the sphere
- Perform tests for 8.13, 8.5, and 9.0% HFC-1234yf concentrations at 20^{o}C, 60^{o}C and 80°C; non-ignitions to be confirmed by nine (9) additional trials

Battery Ignition Apparatus



Battery Ignition Results

- No ignitions observed at 8.13, 8.5, and 9.0% HFC-1234yf at either 20°, 60° or 80°C (10 trials per concentration)
- For comparison the ignitability of ammonia, a refrigerant of relatively low flammability, was tested at a 20% v/v concentration at 20°C and 60° C; positive test was obtained on the first trial

Passenger Compartment Evaluations

- As shown in the previous charts, the flammability parameters were conducted under very tightly controlled conditions.
  - Well mixed, uniform concentration of refrigerant and air.
  - Stagnant, not flowing environment.
  - Fixed conditions (e.g. temperature)
- In actual applications these conditions do not exist.
- Evaluations both experimental and with computer simulations were conducted to try to more closely approximate real world conditions.

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CFD Modeling/Mockup Testing

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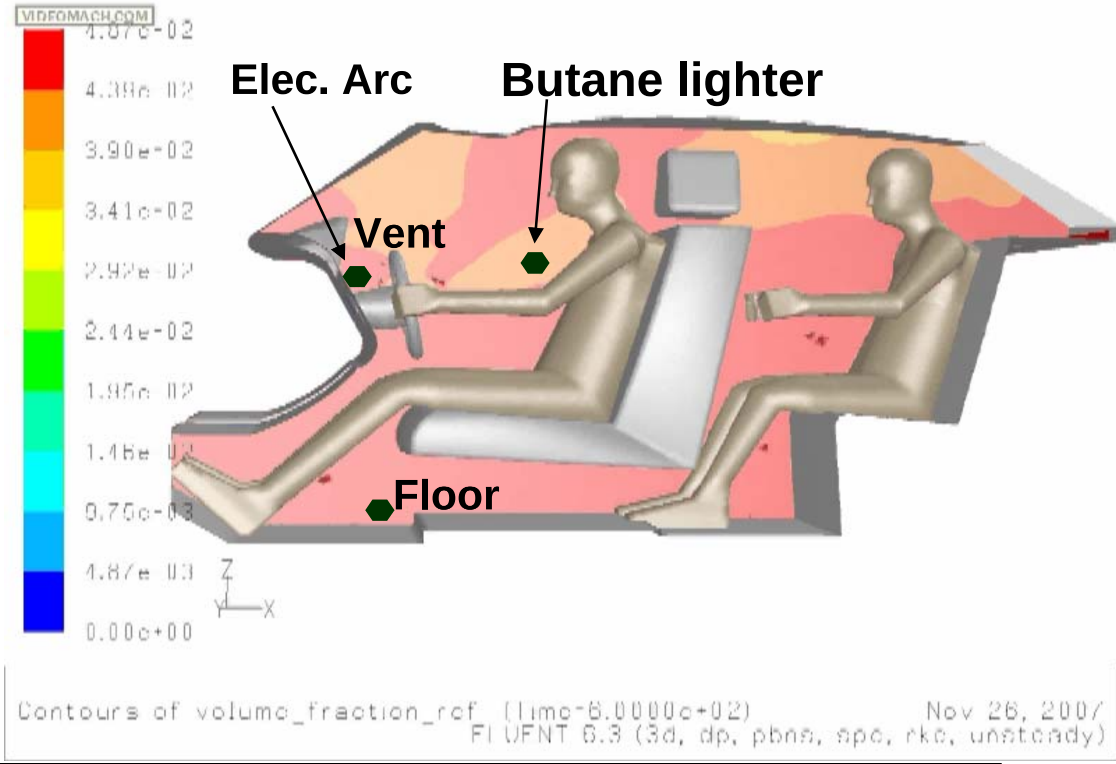
- Good agreement between prediction and measurements.
- No increase in flame length from butane lighter.
- No flame from Electrical Arc.

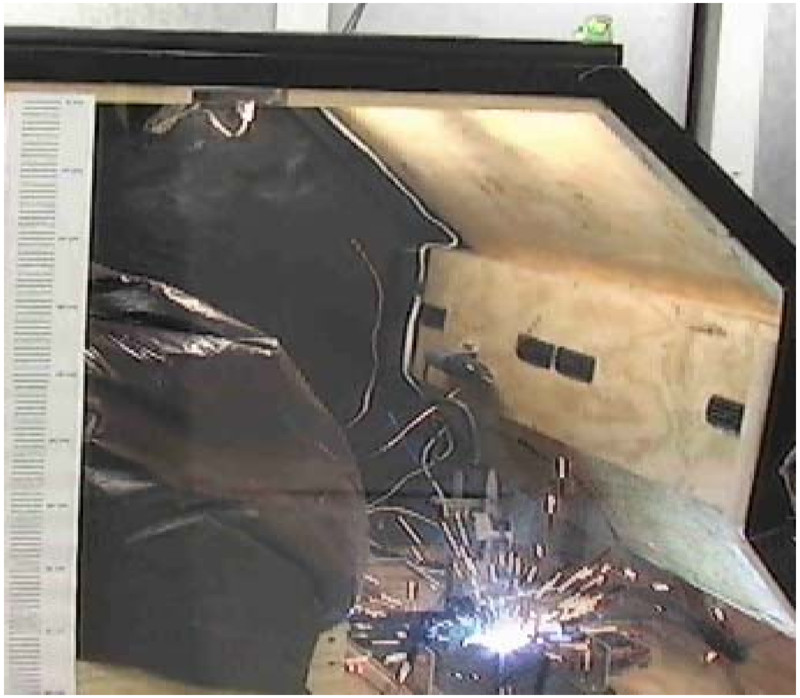


	60 sec		360 sec		600 sec	
	CFD	Test	CFD	Test	CFD	Test
Vent	1.0	0.2	3.5	3.5	4.5	2.4
Floor	1.5	1.4	4.1	3.6	4.5	3.3
Butane Lighter	NO	NO	NO	NO	NO	NO
Elec. Arc	NO	NO	NO	NO	NO	NO

Mock-up Test Example

Extreme Leak Results: No Ignition with Arc Welder

- With simulated ruptured tube leak
  - No ignition with arc welder on floor (simulating battery ignition source)
  - No ignition with arc welder at vent outlet (simulating PTC heater ignition source)



Results of Mock-up Flammability Tests

Deceasing Probability of Occurance ↓

Test No.	Test Description	Ignition Source	Time of Ignition	Result
	Large Corrosion Leak (0.5 mm diameter)			
1	Cigarette lighting at breath level	Butane lighter	After leak starts	No Ignition - only flame color change noted
2	Pooling Test- no blower operation	Arc welder on floor	Four minutes after end of leak	No Ignition
3	Cigarette Lighting at Vent Outlet	Butane lighter	After leak starts	No Ignition - only flame color change noted
	Ruptured Tube Leaks (6.4 mm diameter)			
4	Cigarette lighting at breath level	Butane lighter	After leak starts	Butane lighter failed to light.
5	Simulation of battery short	Arc welder on floor	After leak starts	No ignition
6	Simulation of PTC heater short	Arc welder at vent outlet	After leak starts	No ignition
7	Cigarette Lighting at Vent Outlet	Butane lighter	After leak starts	Butane lighter failed to light.
8	Cigarette lighting at breath level	Butane lighter	At start of leak for entire leak event	Minor flame extension
9	Cigarette Lighting at Vent Outlet Lighter held on for typ lighting time	Butane lighter	At start of leak for 5 secs	No flame extension

CFD Modeling & Flammability Testing Conclusions

- CFD Modeling
  - Good agreement for refrigerant concentration profiles between CFD and mock-up tests
- Mock-up test results
  - Ignition of HFO-1234yf did not occur, even with:
    - worst case leak representing evaporator rupture where LFL was exceeded
    - high energy ignition sources (butane lighter and arc welder)
- Results of hot surface tests at 800 C simulating engine compartment hot manifold showed no ignition.
  - Consistent with engine compartment test results from the CRP-1234 program
- No ignition occurred from 12V battery spark
- This is likely due to low burning velocity and high MIE of HFO-1234yf which makes it difficult to sustain and propagate a flame

HFO-1234yf Flammability Risk is Very Low

Risk Assessments

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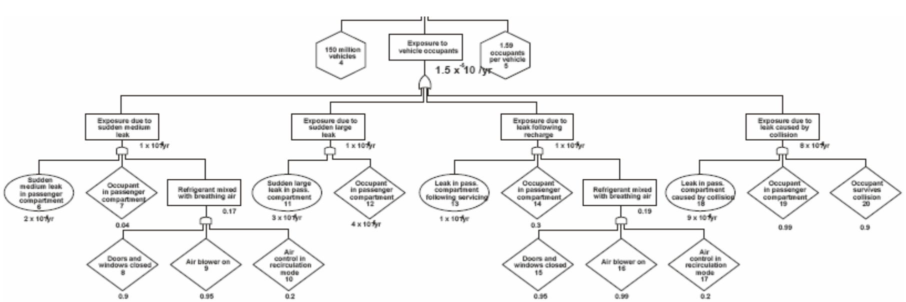
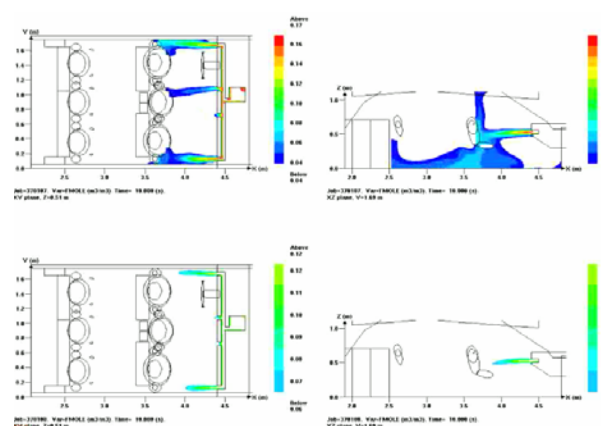
- For most fires to happen, fuel and air at the right <u>concentration</u>, and an ignition source, with a sufficient <u>energy level</u> must co-exist at the <u>same place</u> and in the <u>same time</u>.

- Several risk assessments have been completed or are in progress in US (SAE CRP-1234), Japan (JAMA) and Europe utilizing inputs of modeling and leak experiments

  - ✓ Release Experiments
    - Cabin and underhood
    - Normal operation and crash condition
    - Service (Professional and DIY)

  - ✓ CFD modeling to visualize concentration distribution for various scenarios.





R152a

HFO-1234yf

Table 26. Risks of Injury or Fatality from Various Events Compared to Risks Associated with Leaks of HFO-1234yf

Risk	Risk per year	Citation
Risk of stroke	2.7×10^{-3}	Rhys Williams, 2001
Fatal accident in the home	1.1×10^{-4}	Wilson and Crouch, 1987
Fatal accident while climbing mountains (if mountaineer)	6×10^{-4}	Wilson and Crouch, 1987
Risk of being injured as a pedestrian	2.1×10^{-5}	NSC, 2004
Fatal injury at work (all occupations)	3.6×10^{-5}	NSC, 2004
Injury from lightning strike	1×10^{-6}	NWS, undated**
Risk of being fatally injured in an elevator ride	2×10^{-7}	McCann and Zalesky, 2006
Risk of exposure to HFO-1234yf above health based limits resulting from a collision	$\mathbf{1 \times 10^{-10}}$	CRP1234 Analysis
Risk of being injured by an HFO-1234yf ignition resulting from a collision	$\mathbf{2 \times 10^{-11}}$	CRP1234 Analysis (updated since VDA mtg.)

*Risk cited is 1 in 10,000 over the next century
Injury sufficiently serious to require hospital visit. Based on number of injuries per year divided by total U.S. adult population.
§ Total number of injuries requiring hospital visit per year divided by the total U.S. population.
** Total number of documented injuries from lightning strikes per year, divided by total U.S. population.
& FTA risk multiplied by the number of estimated drivers in the U.S..

Some Key SAE Standards Relevant to HFO-1234yf Under Development

Standard Title	Status	SAE Representative	Working Group
Safety Standards for Motor Vehicle Refrigerant Vapor Compression Systems	Revise J639 -separate different refrigerants into different sections -reviewed in Orlando and sent for ballot	Bill Hill	4
New Ref 152a - 1234yf Recovery/Recycling Equipment and Recovery/Recycling/Recharging for Mobile Air-Conditioning Systems	Revise J2788	Gary Murray	1
New Ref 152a - 1234yf Refrigerant Purity and Container Requirements Used in Mobile Air-Conditioning Systems	Revise J2776	Bill Hill	4
R1234yf Service Standards for Mobile Air Conditioning Systems	Revise J2770	Paul Weissler	5
New Ref 152a - 1234yf Refrigerant Recovery Equipment for Mobile Automotive Air Conditioning Systems [Superseding J1732]	Revise J2210	Gary Murray	1
New Ref 152a - 1234yf Refrigerant Minimum Performance Criteria for Electronic Leak Detectors	Revise J2791	Bill Willams	2
New Ref 152a - 1234yf Ultraviolet Leak Detection minimum requirements for Mobile Air-Conditioning Systems	Revise J2775 or J2297	Phil Trigiani	3
Recommended Service Procedure for the Containment of HFC-152a and HFO-1234yf	Revise J2211	Paul Weissler	5

- First drafts of new Standard Revisions targeted for discussion at SAE ICCC Meeting in April
- Safe Evaporator Standard under consideration.

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Next Steps

- Support OEM property/performance testing
  - Vehicle cooling performance/optimization
  - Compatibility, stability and durability
- Complete toxicity testing
  - Rabbit Developmental exposures complete
    - analysis and final report by August '08
  - Reproductive (preliminary results by August '08)
- Complete regulatory registrations (REACH, SNAP etc)
- Achieve industry consensus on HFO-1234yf as global industry solution by mid'08 and put plans in place to meet 2011 EU MAC Directive.

HFO-1234yf Summary

- **Excellent environmental properties**
  - Very low GWP of 4, Zero ODP, Favorable LCCP
  - Atmospheric chemistry determined and published
- **Low toxicity, similar to R-134a**
  - Low acute and chronic toxicity
  - Significant testing completed
- **System performance very similar to R-134a**
  - Excellent COP and Capacity, no glide
    - From both internal tests and OEM tests
  - Thermally stable and compatible with R-134a components
  - Potential for direct substitution of R-134a
- **Mild flammability (manageable)**
  - Flammability properties significantly better than 152a; (MIE, burning velocity, etc)
  - Potential for “A2L” ISO 817 classification versus “A2” for 152a based on AIST data
  - Potential to use in a direct expansion A/C system - better performance, lower weight, smaller size than a secondary loop system

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