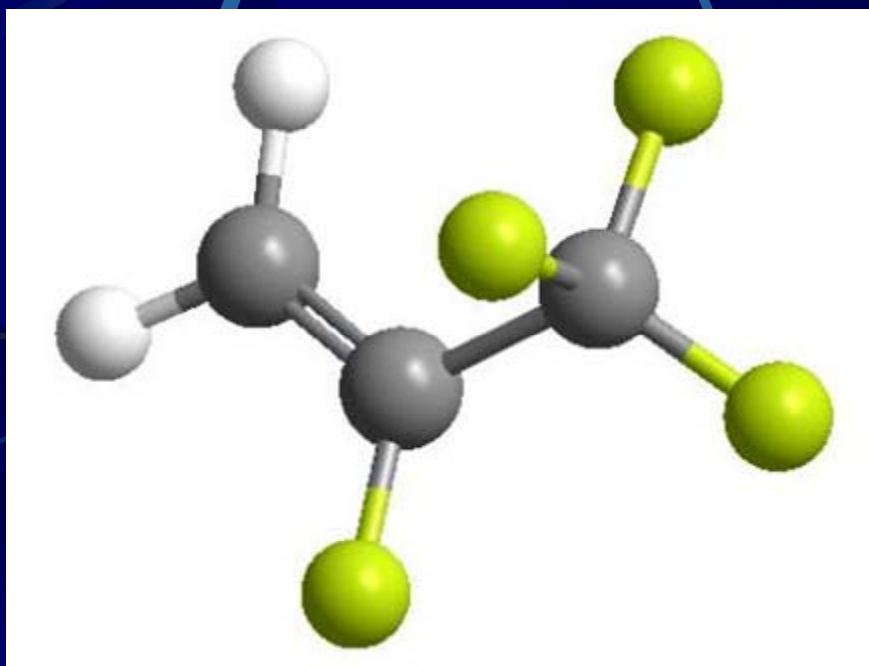


Industry Evaluation of low global warming potential refrigerant HFO-1234yf



SAE CRP1234

HFO-1234yf Cooperative Research Programs

- In 2007, technical experts from global automobile manufacturers and suppliers along with independent test laboratories initiated the SAE Cooperative Research Program CRP 1234 to investigate the safety and performance of HFO-1234yf for use in Mobile Air Conditioning
- Phase 3 of the CRP1234 has completed additional research in 2009

HFO-1234yf Cooperative Research Programs

- Cooperative Research Programs (CRP) have been sponsored by automobile manufacturers and Tier One/Two Suppliers
- Global Vehicle OEMs
 - Audi, BMW, Chrysler, Daimler, Fiat, Ford/Volvo, General Motors/Opel, Hyundai, Porsche, PSA, Renault, Shanghai Automotive, Tata, Jaguar Land Rover, Toyota, VW
- Tier One/Two Suppliers
 - DuPont, Honeywell, Conti Tech, Dayco, Delphi, Denso, Doowan, Dow, Freudenberg, Goodyear, Hutchinson, Maflow, Egelhof, Parker Hannifin, Sanden, Trelleborg, Valeo, Visteon

HFO-1234yf Cooperative Research Programs

- The research, conducted over the last two years at international laboratories to get the best available expertise and to guarantee common worldwide acceptance
- Issues Investigated include:
 - Safety and risk assessment
 - Air-conditioning system efficiency and performance
 - Material compatibility
 - Flammability
 - Toxicity
- Extensive testing at third-party facilities did not identify significant risks for the use of HFO-1234yf in mobile air-conditioning systems.

Safety and Risk Assessment

- Detailed Fault Tree Analysis [FTA] has been completed with input from major OEMs from around the world
- The following scenarios have been considered:
 - Potential risks due to refrigerant flammability
 - Accidental releases during vehicle operation and service
 - Potential risk due to refrigerant toxicity
 - Accidental releases during vehicle operation and service
 - Potential risk due to decomposition products
 - Accidental releases during vehicle operation and service

Safety and Risk Assessment

- **Extensive Fault tree scenarios**
 - **Vehicle use in Field Scenarios**
 - Component Failures
 - Vandalism
 - **Vehicle Collision Scenarios**
 - Occupant
 - Good Samaritan
 - **Service Scenarios**

Risk Comparison to Other Vehicle events

Risks from Various Events Compared to Risks Associated with Leaks of R-1234yf

Risk	Risk per vehicle per operating hour*	Citation
Risk of being in a police reported vehicle collision ¹	5×10^{-5}	NHTSA, 2007
Risk of vehicle collision due to vehicle brake failure ²	3×10^{-7}	New York State DMV
Risk of highway vehicle fire (any cause) ³	1×10^{-7}	Ahrens, 2008; BTS, 2004
Risk of an airbag-related fatality associated with a vehicle collision ⁴	2×10^{-10}	NHTSA, 2001
Risk of vehicle occupant/former occupant experiencing HF exposure above health based limits associated with an R-1234yf ignition event ⁵	3×10^{-12}	Current analysis
Risk of vehicle occupant being exposed to an open flame due to R-1234yf ignition ⁵	9×10^{-14}	Current analysis
Risk	Risk per working hour*	Citation
Non-fatal recordable Injury at work (all occupations) ⁶	2×10^{-5}	NSC, 2004
Risk among automotive repair technicians of being struck by object resulting in lost work days ⁷	2×10^{-6}	BLS, 2007
Risk of recordable incident involving repair technicians being struck with high pressure R-1234yf equipment hose (risk per hour of vehicle service) ⁵	3×10^{-8}	Current analysis
Risk of service technician exposure to an open flame due to R-1234yf ignition ⁵	1×10^{-20}	Current analysis

*Data sources are shown on page 36



Toxicology Assessment of HFO-1234yf

Extensive Toxicity Testing at Leading Labs

- Independent, global testing laboratories have conducted comprehensive toxicity tests on HFO-1234yf
- Based on these tests it is concluded that HFO-1234yf is acceptable for use in mobile air conditioning from a toxicity perspective.

Comparison of HFO-1234yf and R-134a Toxicology

Test	HFO-1234yf	HFC-134a
•Acute Lethality	•LOEL > 400,000 ppm	•LOEL 567,000 ppm
•Cardiac sensitization	•NOEL > 120,000 ppm	•NOEL 50,000 ppm •LOEL 75,000 ppm
•4 week toxicity	•NOAEL 50,000 ppm	•NOAEL > 50,000 ppm
•13 week toxicity	•NOAEL 50,000 ppm	•NOAEL 50,000 ppm
•Genetic Toxicity	•Ames slight activity in 2 strains inactive in 3 others •Chromosome Abberation not active •Micronucleus (mouse) not active •Subacute micronucleus (rat) not active •Unscheduled DNA Synthesis not active	•Ames not active •Chromosome Abberation not active •Micronucleus (mouse) not active
•Developmental Toxicity	•Rat NOAEL maternal 50,000 ppm fetal 50,000 ppm •Rabbit NOAEL maternal 4,000 ppm fetal 7,500 ppm	•Rat NOAEL maternal 30,000 ppm fetal 300,000 ppm •Rabbit NOAEL maternal 2,500 ppm fetal 40,000 ppm
•Reproductive toxicity	•2-Gen NOAEL 15,000 ppm (6-hour exposures)	•NOAEL 50,000ppm (1-hour exp ~8,300ppm x 6hr exp))



INSTITUTES FOR HEALTH SCIENCES

WIL Research Laboratories
The United StatesTNO Pharma
The Netherlands

Toxicology of HF

- HF can be generated when Fluoro-carbon refrigerants decompose
 - Exposure limits for emergency exposures [AEGLs] developed under the National Research Council, supported by the USEPA
 - Agreed upon for use in this setting by an international group of OEM toxicologists
 - Initial warning sign due to strong irritancy
 - Irritancy perception starts at 2-3 PPM
 - HF AEGL-2*:
 - 95ppm / 10 minutes
 - 95ppm also adopted by OEMs for 1 minute exposures [conservative approach]
 - 34ppm / 30 minutes

*Acute Exposure Guideline Level-2

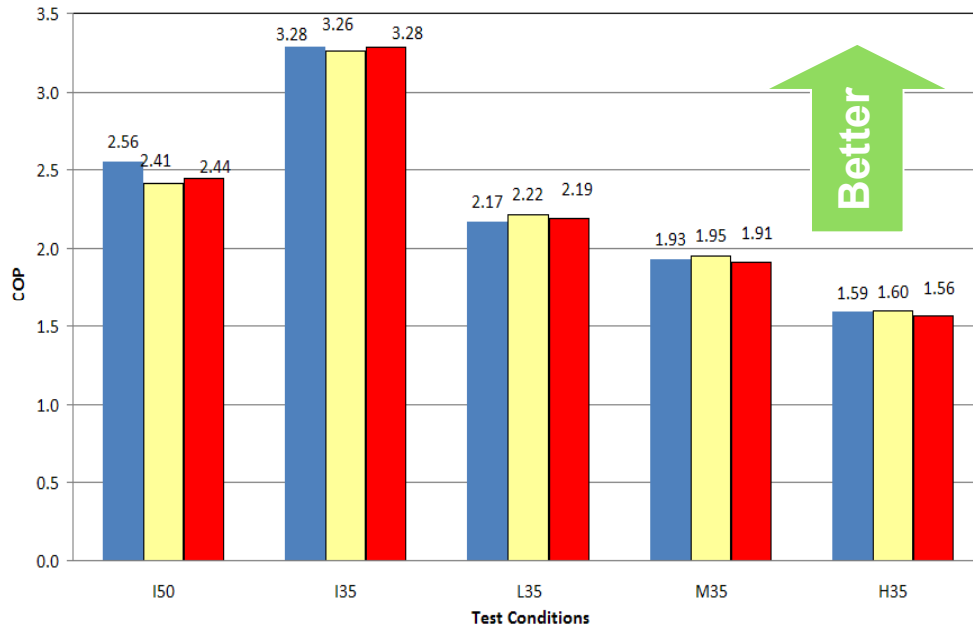
AEGL-2 is the airborne concentration (expressed as ppm or mg/m³) of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

Hydrogen Fluoride Formation

- **Hydrogen fluoride (HF) can be formed when refrigerants containing fluorine are exposed to an open flame or extremely hot surface**
 - Amount of HF generated is highly dependent on the area of exposure, duration, and time of refrigerant contact with the open flame or the hot surface
- **Risk assessments have concluded there is an extremely low probability of ignition of refrigerant associated with HFO-1234yf during an accidental release.**
- **With the application of new safety standards, the specific requirements of HFO1234yf are considered to maintain the safety of the vehicle at today's level**

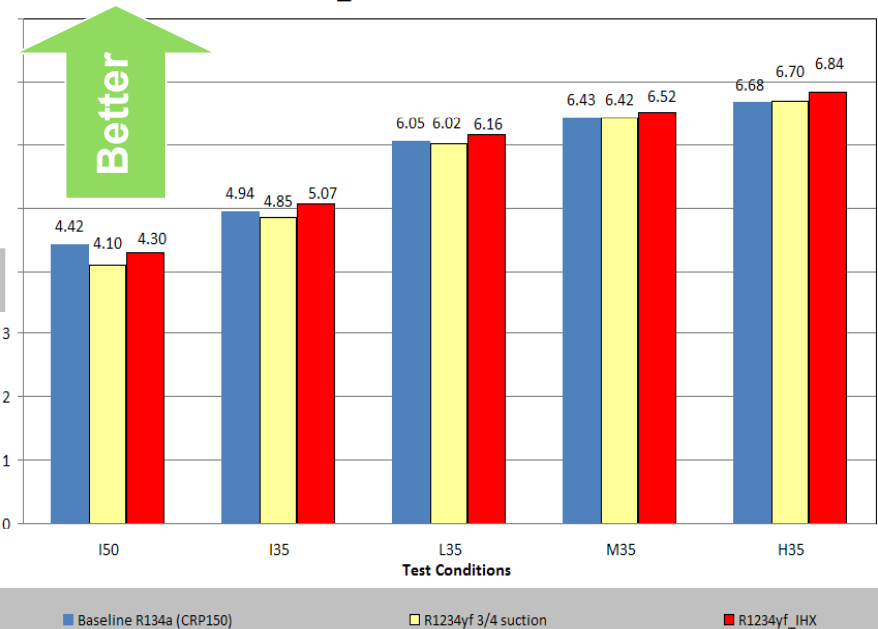
System Capacity and COP

SAE CRP1234 SE R134a vs. HFO-1234yf
COP @ 35C conditions



The comparison to R134a is dependent on the baseline R134a system used for reference

SAE CRP1234 SE R134a vs. HFO-1234yf
Q_{air} @ 35C conditions



cts

Table 1a – Overall Project Summary – Material Compatibility and Permeation*

Material	Compatibility			Permeation	Permeation
	Oil A HFO1234yf	Oil-B HFO1234yf	Oil-C R134a	HFO1234yf	R134a
Seals					
PDM-1					
PDM-2					
PDM-3					
PDM-4					
NBR-1					
NBR-2					
NBR-3					
R-1					
Normal Temp. Hoses					
R-1					
IIR-1					
R-2					
IIR-2					
A-1					
A-2					
High Temp. Hoses					
R-3					
R-4					
R-1					
A-3					
A-4					
A-5					
Thermo-plastics					
PS-1					
PS-2					
EI-1					

Table 1b – Overall Project Summary –Oils*

Oil	Thermal Stability		Miscibility		Daniel Plots	
	R134a	HFO-1234yf	R134a	HFO-1234yf	R134a	HFO-1234yf
Oil-A						
Oil-B						
Oil-C						
Oil-D						

*Green color indicates no issues were noted, Yellow color indicates improvements are suggested, no color indicates materials were not tested

CRP1234-2

Material Compatibility Summary

In all cases some combination of materials is found acceptable

ILK Dresden



Institut für Luft- und Kältetechnik
gemeinnützige Gesellschaft mbH

*Green color indicates no issues were noted, Yellow color indicates some improvements are suggested, no color indicates materials were not tested.

Life Cycle Impact of HFO-1234yf



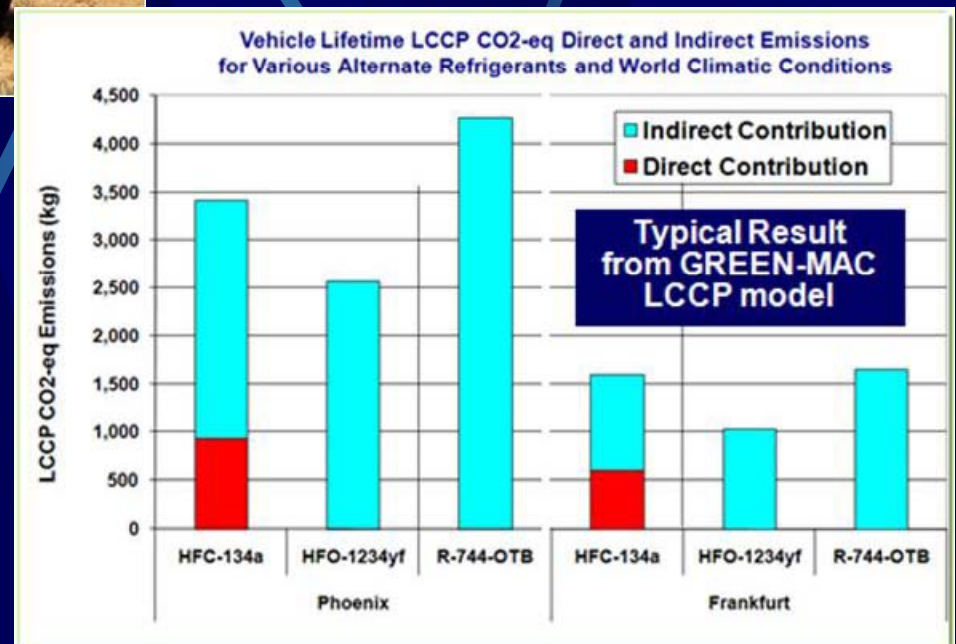
Air conditioning systems derive their power to run from the vehicle's engine, so their efficiency impacts the greenhouse tail pipe exhaust gas emission of the vehicle.

Direct emissions:

The greenhouse gas emissions resulting from the direct emission of the refrigerant.

Indirect emissions:

The greenhouse gas emissions (CO₂) resulting from the power needed to run the air conditioning system. The majority of total GHG emissions come from this, especially for low GWP fluids.



Results are dependent on base system and level of system optimization

In developing a low-GWP solution, one must look at the GHG impact of the refrigerant and its efficiency with an eye on total greenhouse gas emissions

HFO1234yf Flammability Testing

Flammability Testing at Leading Labs

- Flammability testing at Hughes, Ineris, and Exponent labs have demonstrated the difficulty in igniting the HFO-1234yf refrigerant under the most severe testing conditions
- Additional evaluations of refrigerant flammability have been tested in other laboratories [shown in later slides]
- Risk assessment indicates a very low probability that an accidental release of refrigerant creates a sufficient concentration at the same time and location as a sufficient ignition source.
 - Very low probability that occupants could be exposed to an open flame
 - Probability is lower than associated with other hazardous vehicle events [i.e.; brake failure]

HFO-1234yf Flammability Testing

- Ignition Tests
 - Steel vessel
 - Acrylic box
- Engine Compartment
 - Hot surface conditions
- Passenger Compartment
 - Concentration level
 - Ignition sources



Ineris HFO-1234yf Flammability Testing

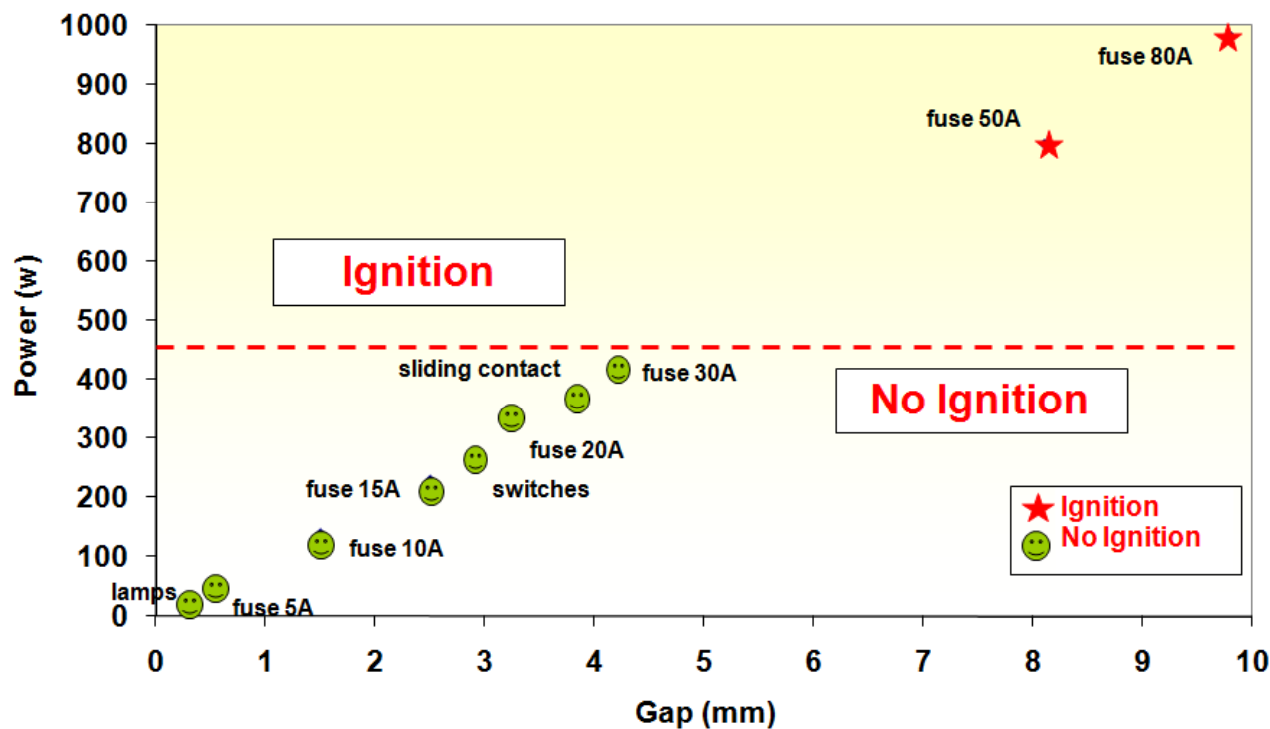
Objective: Understand flammability potential of HFO-1234yf and HFO-1234yf/oil impinging on hot body in engine compartment

- **Test apparatus:** 1m³ box with 50cm² opening in bottom
 - Testing was done without supplemental airflow through the box
 - Temperature range from about 600C to about 1050C
 - Oil level varied from 0 to 7%
- **Results**
 - 7% oil: Ignition @ 750C (no ignition until that temp is reached)
 - 3% oil: Ignition @ 750C (no ignition until that temp is reached)
 - HFO-1234yf without oil does not ignite until temperature exceeds 1000C



Ineris Potential Ignition Sources for HFO-1234yf

Potential Ignition Sources Investigated



HFO-1234yf Ignition Source Testing Under Ideal Static Laboratory Conditions*

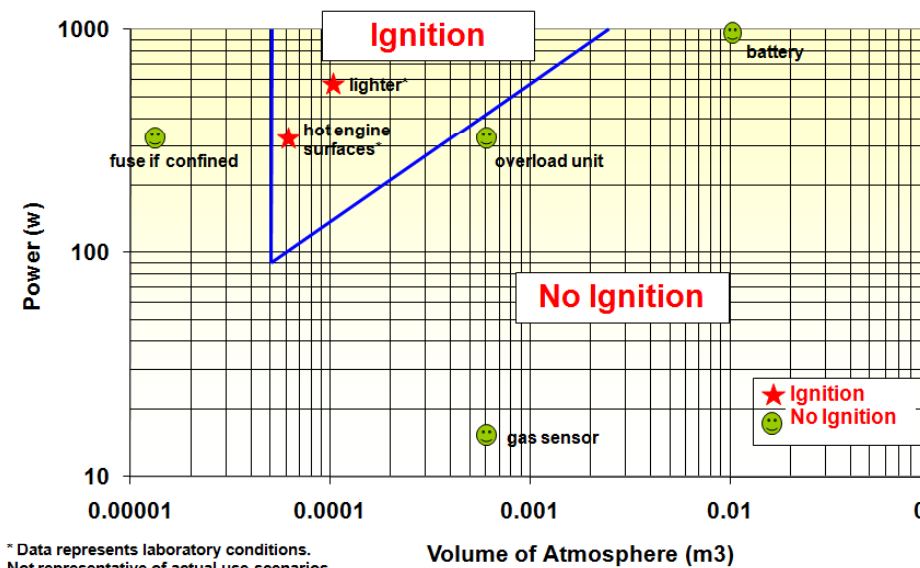
Ignition Source	Ignition Occurred?
Battery 12 Volt	No
Control Switches	No
Friction	No
Fuse 5 Amp	No
Fuse 10 Amp	No
Fuse 15 Amp	No
Fuse 20 Amp	No
Fuse 30 Amp	No
Fuse 50 Amp	Yes
Fuse 80 amp	Yes
Lamps Sliding Contacts	No
Lighter	Yes
Loose Contacts	No
Overload Unit	No
Power Switches	No
Toxicity Sensor	No

Ineris testing found very few potential ignition sources within vehicle.

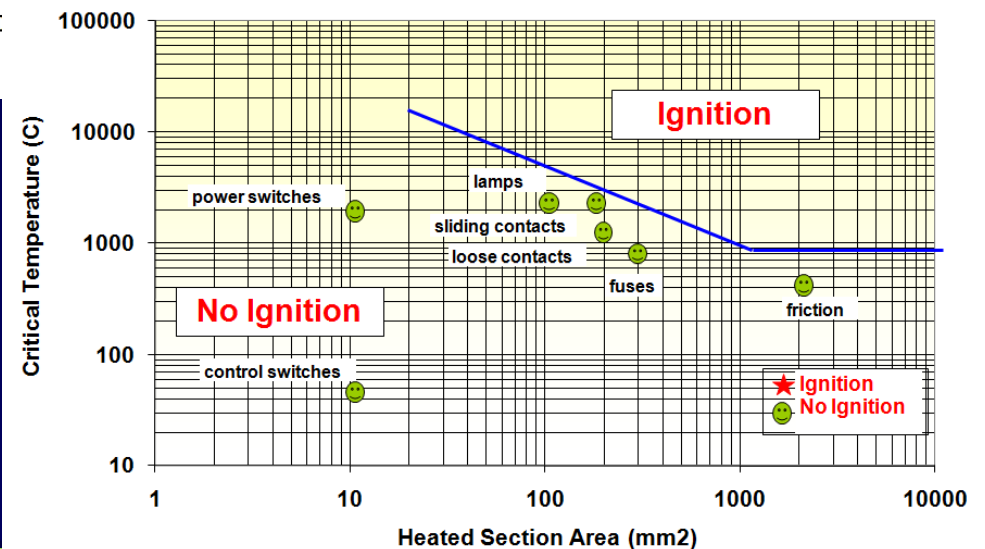


Ineris Potential Ignition Sources for HFO-1234yf

Potential Ignition Sources Investigated



Potential Ignition Sources Investigated



Ineris Potential HF Generation from HFO-1234yf on Hot Body

- HF production is proportional to heated area where refrigerant impinges and strongly influenced by the temperature of hot body
- HF product is also influenced by addition of oil
- HF concentration increases as a function of time when HFO or R134a stays in hot body vicinity



Testing with HFO-1234yf at Hughes Associates, Inc.

- **Air Samples Analyzed for Hydrogen Fluoride (HF) with Ion Specific Electrode (ISE) Technique**
 - Interior and underhood surfaces [dermal contact surfaces]
- **Passenger Compartment Testing**
 - Benzomatic Lighter Used to Decompose Refrigerant
 - Lighter Placed at Simulated Cigarette Smoking Area
 - HF Measurements at Driver's Breath Zone
- **Engine Compartment Testing**
 - Heated Tube Section Placed Underhood Used to Decompose Refrigerant Mixed with Compressor Oil (3% by wt)
 - Simulated High Temperature Surfaces Near Cabin Air Inlet (450°C and 700°C)
 - HF Measurements at Driver's Nose, HVAC Module, Cabin Air Inlet & Engine Compartment

Cigarette Smoking Test

There were no significant differences in the amount of HF formed during inhalation of either R-134a or HFO-1234yf through a cigarette. The HF values found during this investigation were very low (less than 10 ppm).

(With refrigerant concentrations up to 2%)

R-134a has been used for over 16 years within the automotive industry as a mobile air-conditioning refrigerant.

**Massachusetts
smoking simulator**

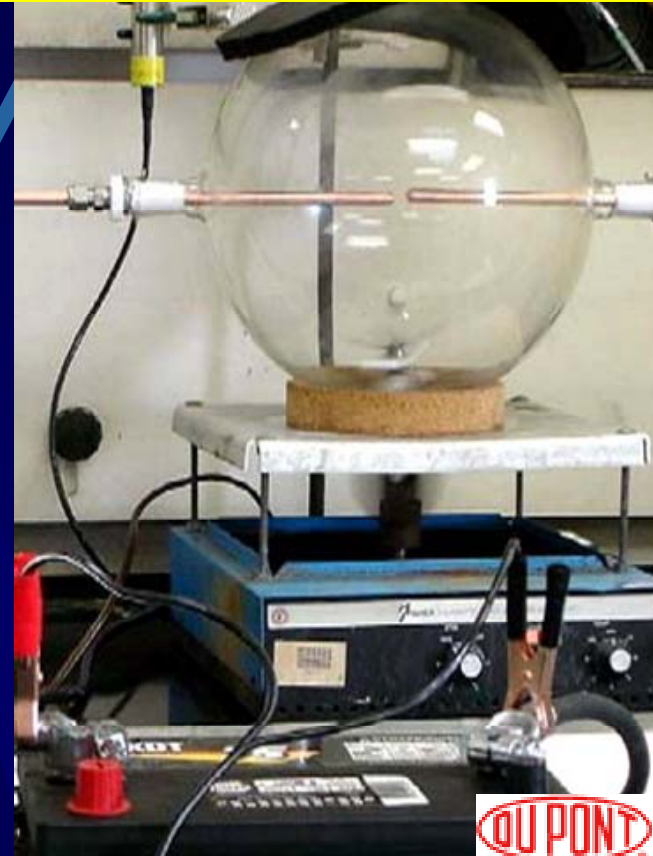


The miracles of science™

Spark Testing with HFO1234yf

- Well-blended R1234yf/air mixture
 - Known concentration in a sealed 12-l spherical flask
 - Moisture equivalent to 50% RH at 23C
- 9.5 mm diameter copper electrodes located in the flask
 - Short-circuit of 12-Volt automotive battery (1020 cranking amps) in the mixture

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



The miracles of science™

Battery Short Testing with HFO1234yf

- Sparks Generated
- No evidence of HFO-1234yf ignition
- Tests for 8.13, 8.5, and 9.0 vol % in air, HFO-1234yf
- Concentrations at 20 and 60C

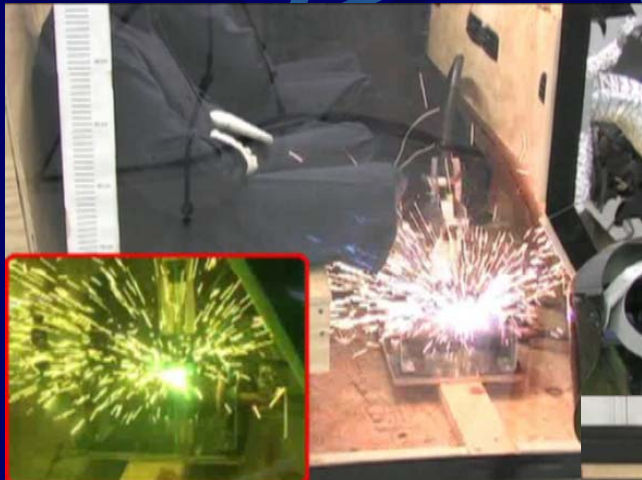
HFO-1234yf Ignitability to Spark from
12-Volt Battery Short Circuit

NO IGNITION OBSERVED



The miracles of science™

Ignition testing in a vehicle mock-up with HFO-1234yf



Simulated battery short
NO IGNITION of refrigerant



Lighter at Vent Outlet
Lighter fails to operate above 4 vol%


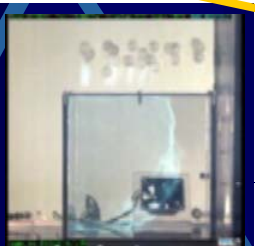
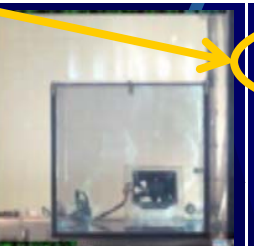


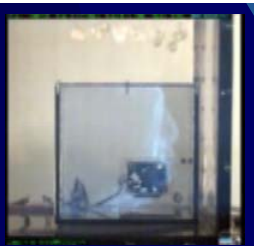
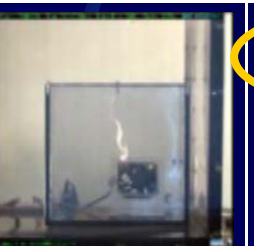

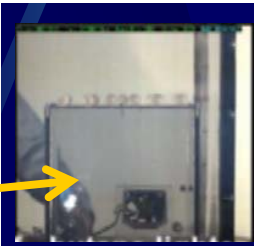

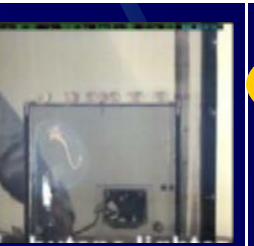
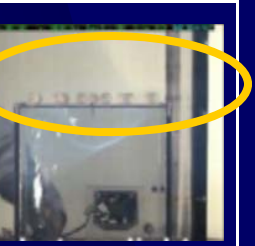


Cigarette lighting at breath
Minor flame extension, NO IGNITION

Honeywell

Visualization of Pressure Rise on Ignition

Watch the ping pong balls for pressure rise.

	t = 63 ms	125 msec	250 msec	500 msec
Isobutane Elect. Arc - ignition 4 vol%				
R-152a Elect. Arc - ignition 8 vol%				
HFO-1234yf Elect. Arc – no ign Lighter – above 4 vol%, no ign Elect. Arc + butane → ign 8 vol%, orange flame is butane				

Honeywell

Atmospheric effects

The following impacts have been considered:

- Climate change
- Stratospheric ozone
- Local air quality
- Ecosystems (formation of noxious/toxic degradation products)

Impact on Climate Change

**Degradation is initiated by reaction with OH radicals
[1, 2, 3]**

Atmospheric lifetime is 11-12 days [1,3]

GWP estimates of 4 and <4.4 [1,3]

Atmospheric lifetime and GWP of HFO-1234yf are well established. No significant contribution to radiative forcing of climate change.

References

1. O.J. Nielsen, M.S. Javadi, M.P. Sulbaek Andersen, M.D. Hurley, T.J. Wallington, R. Singh, Chem. Phys. Lett., 439, 18 (2007);
2. V. L. Orkin, R. E. Huie and M. J. Kurylo, J. Phys. Chem. A, 1997, 101, 9118–9124; 3.
3. V.C. Papadimitriou, R.K. Talukdar, R.W. Portman, A.R. Ravishankara, J.B. Burkholder, Phys. Chem. Chem. Phys., 10, 808 (2008).

Impact on Stratospheric Ozone

HFO-1234yf does not contain chlorine or bromine and hence will not contribute to the well-established Cl- and Br-based catalytic ozone destruction cycles.

HFO-1234yf has ODP = 0.

Impact on Local Air Quality

Using method of Jenkin (1998), the photochemical ozone creation potential (POCP) for HFO-1234yf is estimated to be 7 and lies between those for methane (0.6) and ethane (12.3).

Methane and ethane are considered unreactive with respect to local air quality issues and are exempt from air quality regulations.

The claim that “HFO-1234yf has a POCP comparable to ethylene” in EPA-HQ-OAR-2008-0664 NPRM is incorrect. Ethylene has a POCP = 100 (14 times greater than that for HFO-1234yf).

HFO-1234yf will not impact local air quality (ozone).

Jenkin, M.E., Photochemical Ozone and PAN Creation Potentials: Rationalisation and Methods of Estimation, AEA Technology plc, Report AEAT-4182/ 20150/003, 1998

Trifluoroacetic Acid Formation

Atmospheric oxidation of HFO-1234yf gives $\text{CF}_3\text{C}(\text{O})\text{OH}$ (TFA) in 100% molar yield.

Trifluoroacetic acid is a ubiquitous natural component of the hydrosphere [1,6,7,8,9,11]. Trifluoroacetic acid is biodegradable [10] and does not bioaccumulate in animals or lower aquatic life forms [4,11].

For emission of <50 kt HFO-1234yf per year uniform mixing, and $4.9\text{E}17$ L annual global precipitation, the global average TFA concentration in precipitation will be <100 ng/L. Majority of emissions will be in N. Hemisphere, so N. Hemispheric average will be <200 ng/L. Reported TFA levels in precipitation in North America in 1998-2004 lie in range 3-2400 ng/L [7]. HFO-1234yf degradation is not expected to have significant impact on environmental loadings of TFA.

Tang et al. (1998) conclude “no significant risk is anticipated from TFA produced by atmospheric degradation of the present and future production of HFCs and HCFCs as there is a 1000-fold difference between the PNEC (Predicted No Effect Concentration) and the PEC (Predicted Environmental Concentration)”.

Benesch et al. (2002) studied impact of 10-10000 $\mu\text{g/L}$ TFA on vernal pool and wetland plant species, no effect was observed, conclusion was “predicted TFA concentrations will not adversely affect the development of soil microbial communities and vernal pool plant species”. Note TFA concentrations used were more than 50-50,000 times greater than N. Hemispheric average estimate above for HFO-1234yf degradation.

WMO (2007) conclude “... trifluoroacetic acid from the degradation of HCFCs and HFCs will not result in environmental concentrations capable of significant ecosystem damage”.

Hurley et al. (2008) conclude that “the products of the atmospheric oxidation of HFO-1234yf have negligible environmental impact”.

Trifluoroacetic acid formation from HFO-1234yf will not impact ecosystems.

References

[1] Berg et al, *Environ. Sci. Technol.* 34, 2675-2683, 2000; [2] Benesch et al. *Environ. Tox. Chem.*, 21, 640, 2002; [3] Hurley et al., *Chem. Phys. Lett.*, 450, 263 (2008); [4] Tang, et al., *J. Photochem. Photobiol.*, B 46, 83, (1998); [5] WMO, Scientific Assessment of Stratospheric Ozone: 2006, World Meteorological Organization, Geneva (2007); [6] Frank et al., *Environ. Sci. Technol.* 36, 12-15, 2002. [7] Scott, et al., *Environ. Sci. Technol.*, 40, 7167-7174, 2006; [8] Scott, et al., *Environ. Sci. Technol.*, 39, 6555-6560, 2005; [9] Von Sydow et al., *Environ. Sci. Technol.*, 34, 3115-3118, 2000. [10] Kim et al., *Environ. Eng. Sci.*, 17, 337, 2000. [11] Boutonnet et al. *Human Eco. Risk Assess.* 5, 59 1999.

Atmospheric effects

Should we be concerned that HFO-1234yf will impact:

- **Climate change** -- No
- **Stratospheric ozone** -- No
- **Local air quality** -- No
- **Ecosystems** -- No

New ISO and SAE HFO-1234yf Standards

(Under development or revision to be published)

ISOTC 22 N 2916 ISO/CD 13043 Road Vehicles-Refrigerant systems used in Mobile Air Conditioning systems [MAC]-Safety Requirements

J639 Safety Standards for Motor Vehicle Refrigerant Vapor Compression Systems

J2064 R134a and HFO-1234yf Refrigerant Automotive Air-Conditioning Hose and Assemblies

J2065 Desiccant Testing for Vehicle Air conditioning Systems

J2772 Measurement of Passenger Compartment Refrigerant Concentrations under system refrigerant leakage conditions

J2773 HFO-1234yf and R744 Refrigerant Standard for Safety and Risk Analysis for use in Mobile Air Conditioning Systems

J2842 HFO-1234yf and R744 Design Criteria and Certification for OEM Mobile Air Conditioning Evaporator and Service Replacements

J2843 HFO-1234yf Recovery/Recycling/Recharging Equipment for Flammable Refrigerants for Mobile Air-Conditioning Systems

J2844 HFO-1234yf New Refrigerant Purity and Container Requirements Used in Mobile Air-Conditioning Systems

J2845 Technician Training for Safe Service and Containment of Refrigerants Used in Mobile A/C Systems (R-744, and HFO-1234yf)

J2851 HFO-1234yf Refrigerant Recovery Equipment for Mobile Automotive Air-Conditioning Systems

J2888 HFO-1234yf Service Hose, Fittings and Couplers for Mobile Refrigerant Systems Service Equipment

J2911 Certification Requirements For Mobile Air Conditioning System Components, Service Equipment, and Service Technicians to Meet SAE J Standards

J2912 HFO-1234yf Refrigerant Identification Equipment for Use with Mobile Air Conditioning Systems

J2913 HFO-1234yf Refrigerant Electronic Leak Detectors, Minimum Performance Criteria

Conclusion

The sponsors of the SAE CRP1234 have concluded that HFO-1234yf can be used as the global replacement refrigerant in future mobile air conditioning systems and it can be safely accommodated through established industry standards and practices for vehicle design, engineering, manufacturing, and service.

REFERENCES

References for Comparative Risks

- ¹ There were 6,024,000 police reported vehicle collisions in the U.S. in 2007. This is divided by the number of registered vehicles (255,748,000, NHTSA 2009) and the average number of hours each vehicle is operated (approximately 500 hours based on SAE J2766, Table 6).
- ² The New York State Department of Motor Vehicles reports 1753 accidents in 2008 attributed to brake failure (NYSDMV, 2008) and roughly 11 million registered vehicles in New York State in 2008. Combining these data with the "operating hours per year" suggested in J2766 (~500 as an average) yields the an accident frequency per vehicle operating hour.
- ³ Ahrens reports that 33 highway vehicle fires are reported per hour. This is divided by the number of registered vehicles in the U.S. (255,748,000, NHTSA 2009) .
- ⁴ Based on NHTSA statistics for 1990 to 2001, the average number of confirmed air-bag related fatalities per year is 16. This is divided by the number of hours of vehicle operation per year (approximately 500 hours based on SAE J2766, Table 6) and the number of vehicle drivers in the U.S. (200 million) to arrive at an average hourly risk rate.
- ⁵ FTA estimated risk.
- ⁶ The rate (3.7 per 100 workers) for non-fatal workplace injuries reported for 2008 by the U.S. Bureau of Labor Statistics (BLS, 2008) divided by the number of working hours per year in the U.S. (*i.e.*, 2080).
- ⁷ The U.S. Bureau of Labor Statistics (2007) reports a total of 3450 cases in 2005 of automotive repair technicians and mechanics being struck by an object at work resulting in an injury that required time off from work. This can be divided by the number of technicians and mechanics working in the U.S. (954,000, BLS, 2007) and 2,080 working hours per year to yield a risk per working hour.
- * Risks are given in these units to be consistent with international performance standards used by the automotive industry. Results of the Phase I and Phase II risk assessment were given in risks per year. Conversion between these units is possible by accounting for the number of vehicle operating hours per year (roughly 500 hours) and the size of the relevant vehicle fleet (e.g., roughly 250 million vehicles in the U.S.). Note that the outcomes of individual fault trees should not all be combined because some have different denominators (events per vehicle operating hour, events per year). The values shown here represent the highest estimates when combining individual fault trees with common units of the top level events.