HFO-1234yf Low GWP Refrigerant: A Global Sustainable Solution for Mobile Air Conditioning

Honeywell / DuPont Joint Collaboration

Mark Spatz   *Barbara Minor*

SAE 2008 Alternate Refrigerant Systems Symposium, June 10-12, 2008, Scottsdale, AZ

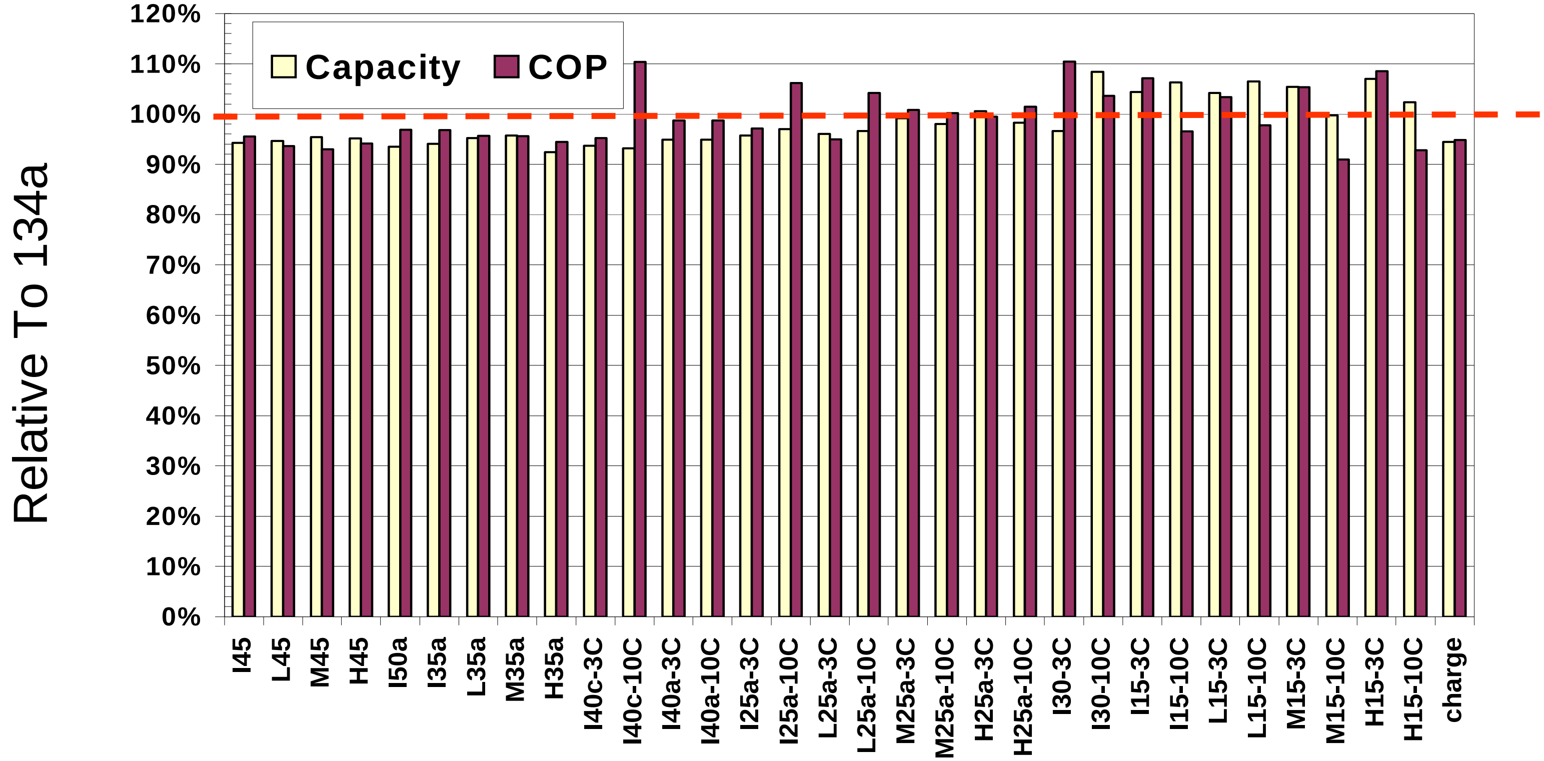
Agenda

- Performance Optimization Tests
- HFO-1234yf Properties
  - Toxicity
  - Environmental
  - Water solubility/Electrical
  - Desiccant compatibility
- HFO-1234yf Handling/Supply Chain
- Path Forward

HFO-1234yf Overview

- **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
- **Global Solution**
  – Lowest total cost of transition than any alternative
  – good performance in all climates, and car sizes

System Bench Test Results



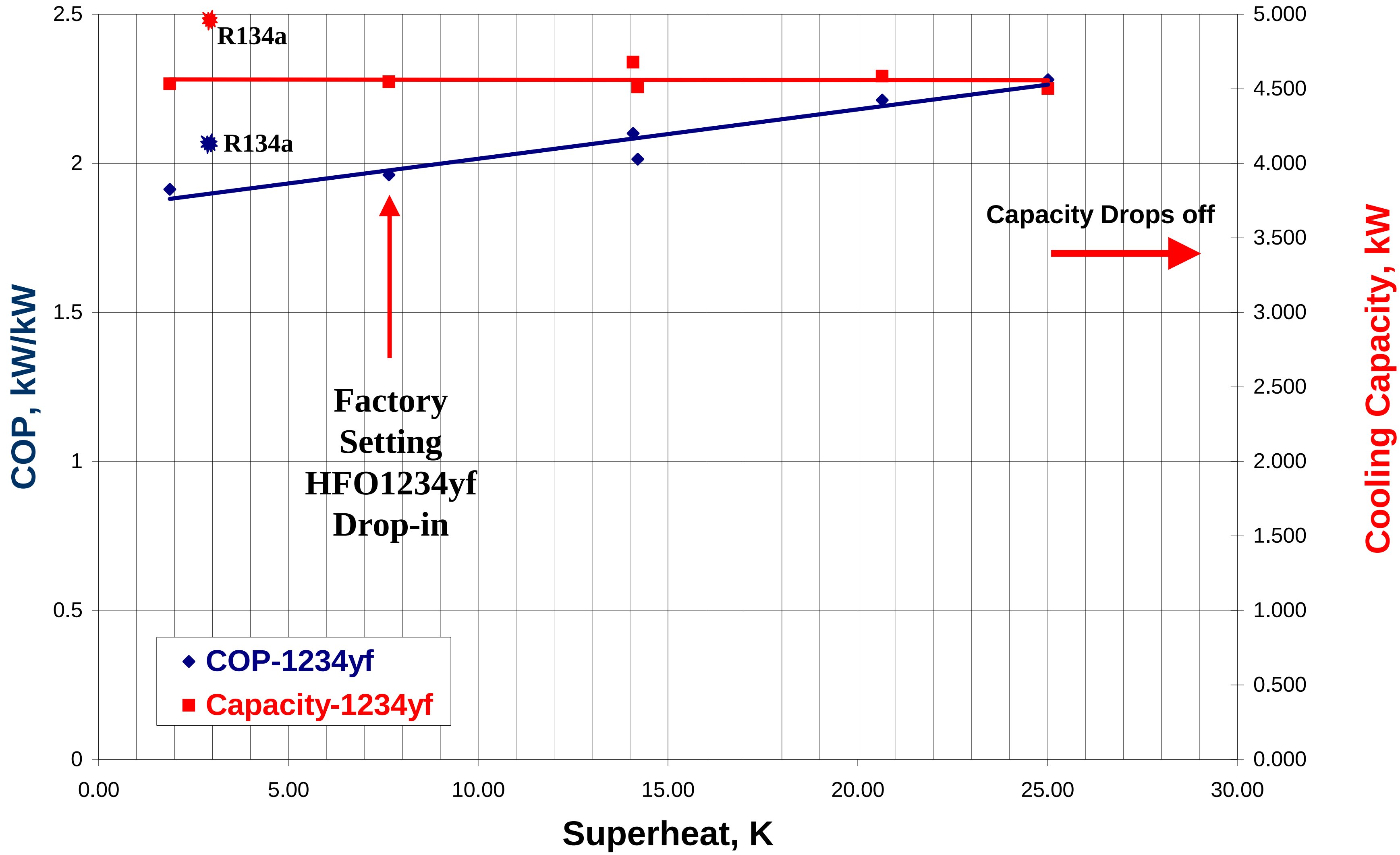
- No changes were made to system including TXV; Industry standard test conditions
- Both Capacity and COP are generally within 5% of 134a performance.
  - This was recently confirmed at two outside labs.
- Lower compression ratio, low discharge temperature (12°C lower at peak conditions)
- Further improvements 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

DuPont The miracles of science™

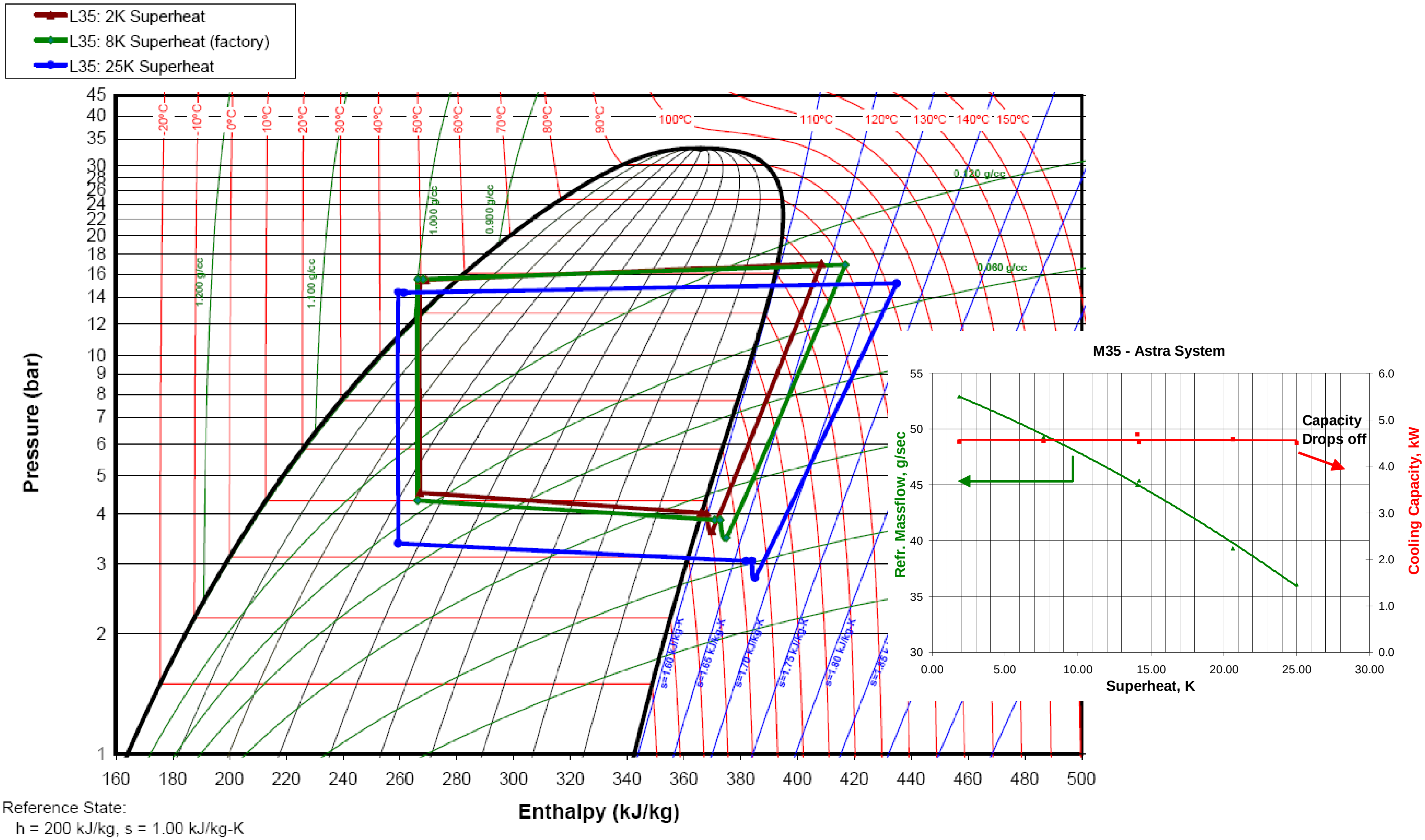
Superheat Study – Capacity and COP (L35)

Honeywell



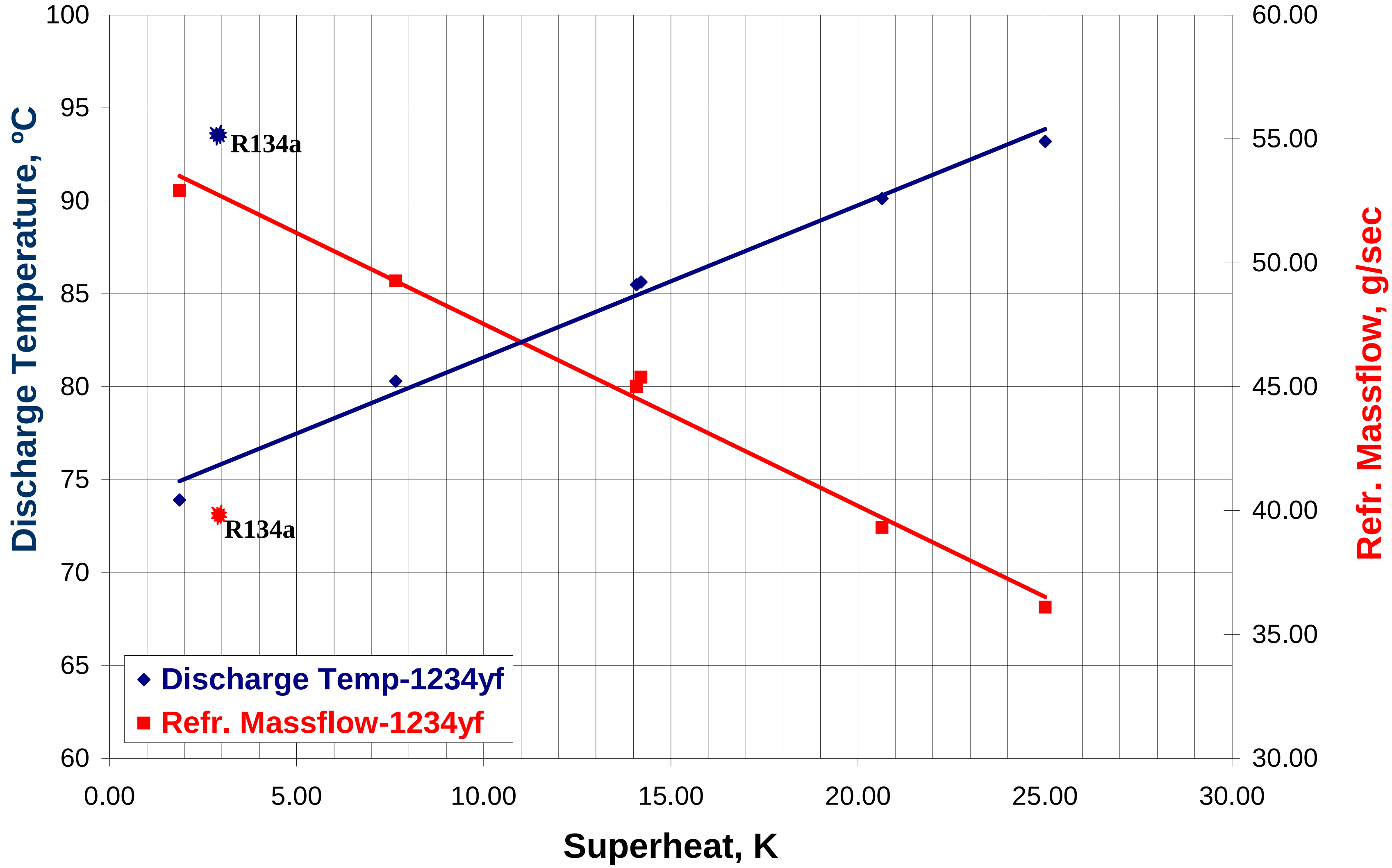
Significant COP Improvement with Optimized SH

Superheat Study – PH Diagram



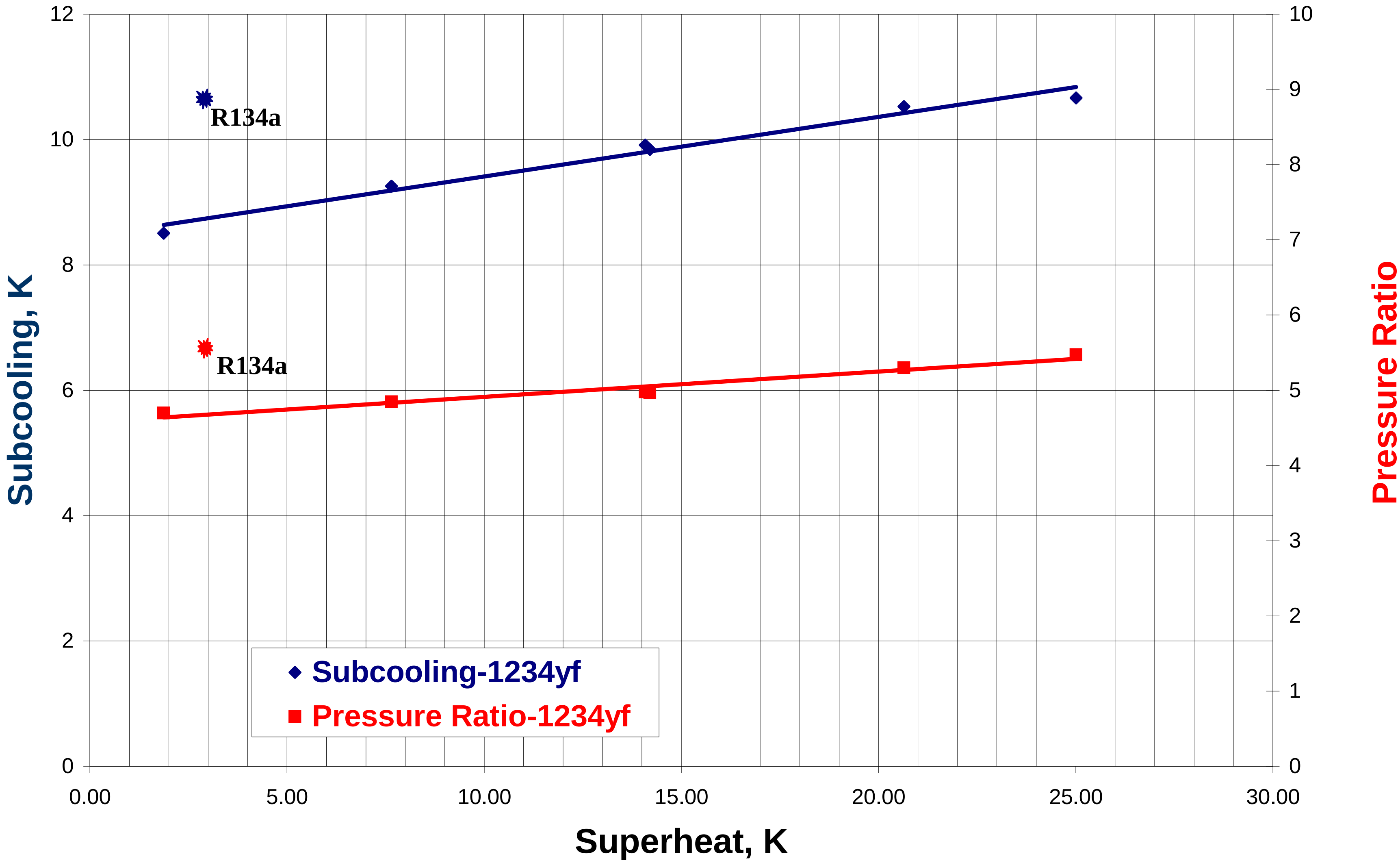
Reference State:
h = 200 kJ/kg, s = 1.00 kJ/kg-K
sat. liq at 0 ºC

Superheat Study – Mass Flow and Discharge T



Optimized Superheat Return Parameters to R-134a Levels

Superheat Study – Subcool and Pressure Ratio



Optimized Superheat Return Parameters to R-134a Levels

Sanden HFO-1234yf Optimization Bench Tests

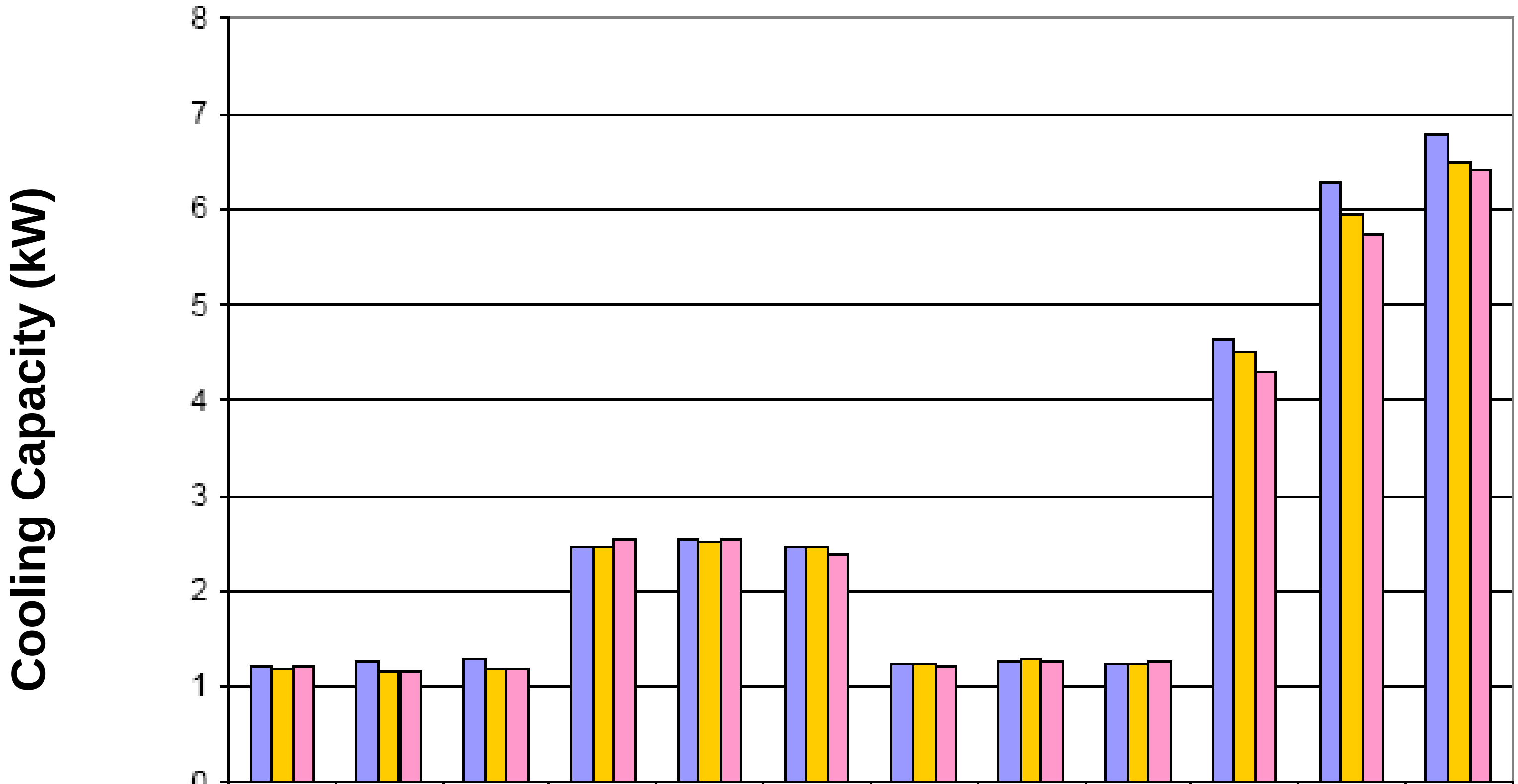
- Tests conducted
  - R-134a Baseline
  - HFO-1234yf drop-in with no changes
  - HFO-1234yf with TXV adjustment
  - HFO-1234yf with modified TXV by Fujikoki

Sanden Test Matrix

Test Condiitions

Point	n_V [1/min]	t_{CL1} [℃]	t_{0L1} [℃]	m_{CL} [kg/h]	m_{0L} [kg/h]	φ_{oL1} [% rel.H.]	Target Temperature
1.1	800	25	25	750	175	50	t_{0L2}=8℃
1.2	1500	25	25	1200	175	50	t_{0L2}=8℃
1.3	2500	25	25	2200	175	50	t_{0L2}=8℃
2.1	800	25	25	750	350	50	t_{0L2}=8℃
2.2	1500	25	25	1200	350	50	t_{0L2}=8℃
2.3	2500	25	25	2200	350	50	t_{0L2}=8℃
3.1	800	40	25	750	175	50	t_{0L2}=8℃
3.2	1500	40	25	1200	175	50	t_{0L2}=8℃
3.3	2500	40	25	2200	175	50	t_{0L2}=8℃
4.1	800	40	40	750	350	50	max PWM
4.2	1500	40	40	1200	350	50	max PWM
4.3	2500	40	40	2200	350	50	max PWM

Sanden Test Results - Capacity



	1,1	1,2	1,3	2,1	2,2	2,3	3,1	3,2	3,3	4,1	4,2	4,3
R134a	1,21	1,26	1,28	2,48	2,54	2,48	1,25	1,26	1,23	4,64	6,28	6,78
R1234yf	1,18	1,16	1,19	2,48	2,52	2,47	1,24	1,29	1,24	4,52	5,94	6,49
R1234yf TXV	1,20	1,17	1,18	2,56	2,54	2,40	1,21	1,26	1,27	4,30	5,74	6,41

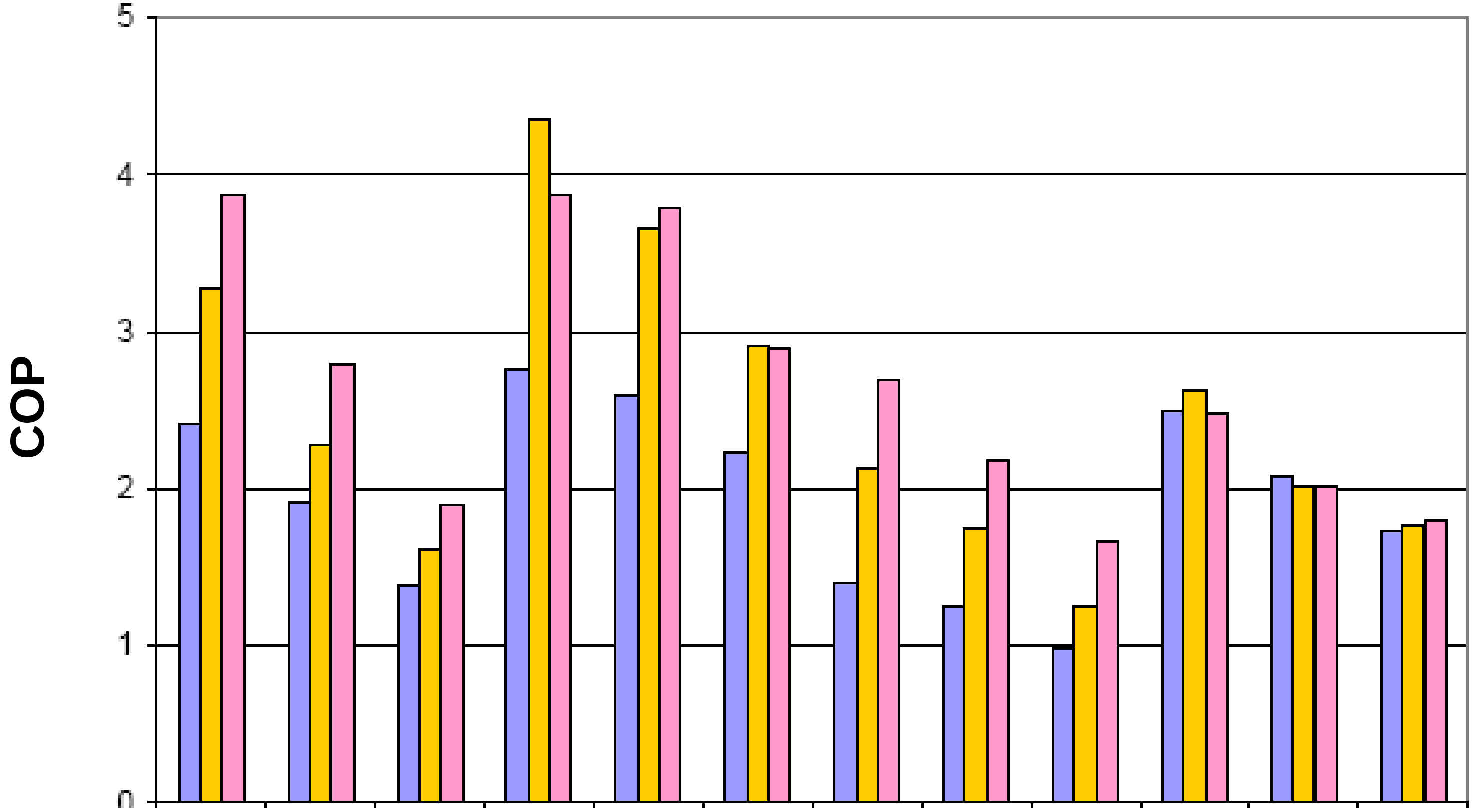
Cooling capacity similar to R-134a

Delivering Excellence

Sanden Test Results - COP

DuPont — The miracles of science™

Honeywell

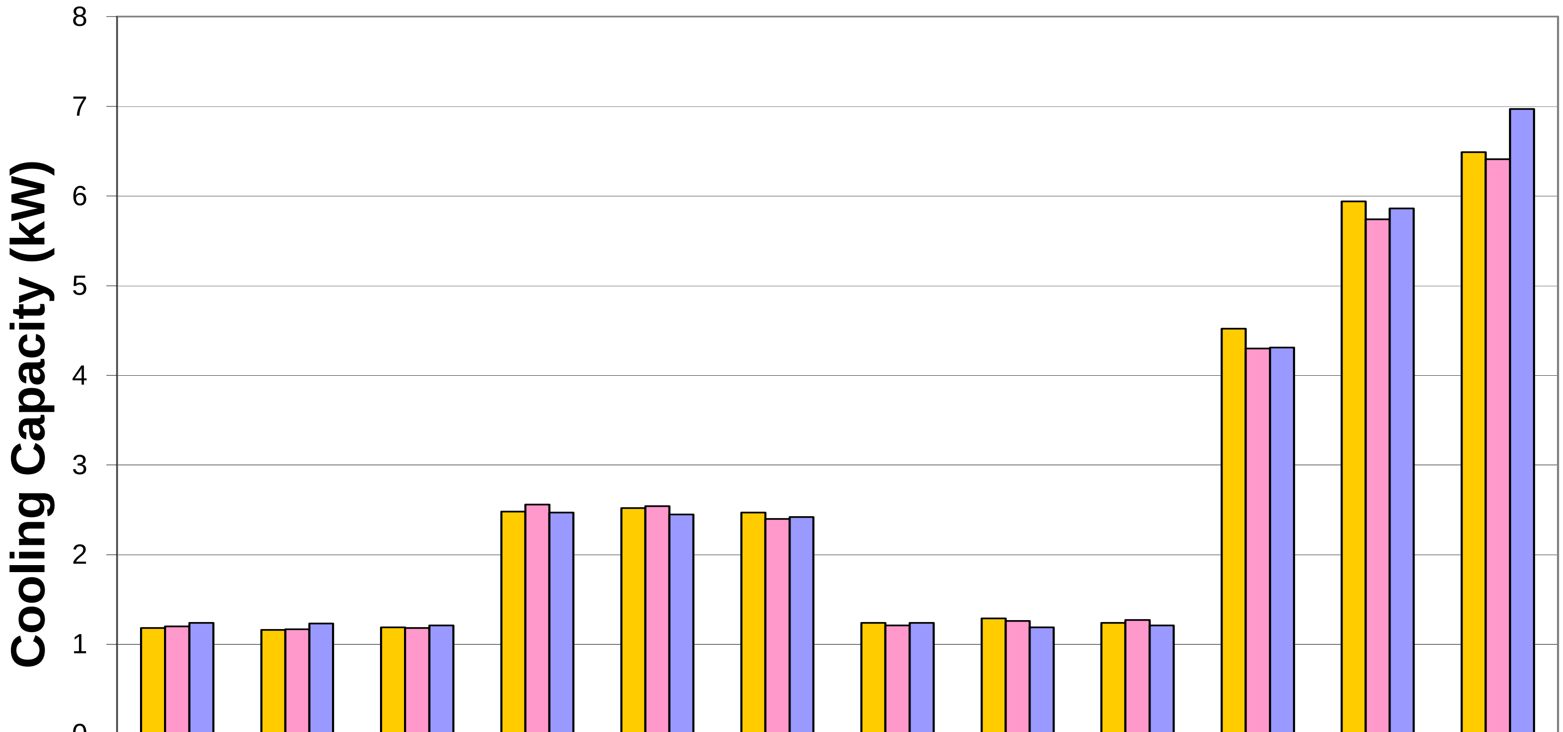


	1,1	1,2	1,3	2,1	2,2	2,3	3,1	3,2	3,3	4,1	4,2	4,3
R134a	2,42	1,91	1,39	2,76	2,59	2,23	1,40	1,25	0,99	2,49	2,07	1,74
R1234yf	3,28	2,27	1,61	4,35	3,65	2,91	2,14	1,74	1,25	2,63	2,02	1,76
R1234yf TXV	3,87	2,79	1,90	3,88	3,79	2,89	2,69	2,17	1,67	2,49	2,01	1,81

COP improved versus R-134a

SANDEN
Delivering Excellence

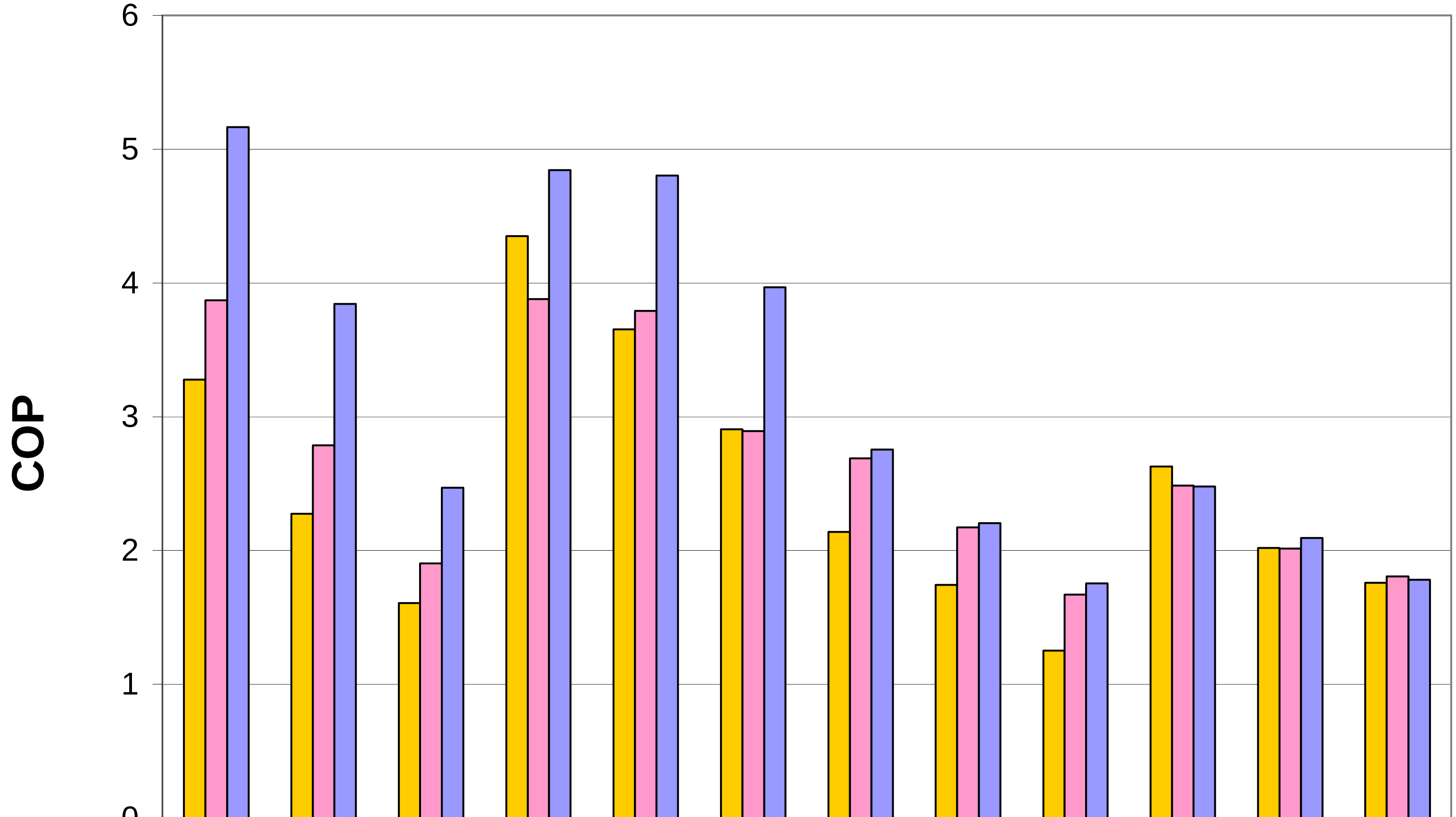
Sanden Bench Test – Capacity with modified TXV



	1,1	1,2	1,3	2,1	2,2	2,3	3,1	3,2	3,3	4,1	4,2	4,3
Original TXV	1,18	1,16	1,19	2,48	2,52	2,47	1,24	1,29	1,24	4,52	5,94	6,49
TXV modi. manual	1,20	1,17	1,18	2,56	2,54	2,40	1,21	1,26	1,27	4,30	5,74	6,41
TXV 2.0t Fujikoki	1,24	1,23	1,21	2,47	2,45	2,42	1,24	1,19	1,21	4,31	5,86	6,97

Cooling capacity similar to R-134a

Sanden Bench Test – COP with modified TXV



	1,1	1,2	1,3	2,1	2,2	2,3	3,1	3,2	3,3	4,1	4,2	4,3
Original TXV	3,28	2,27	1,61	4,35	3,65	2,91	2,14	1,74	1,25	2,63	2,02	1,76
TXV modi. manual	3,87	2,79	1,90	3,88	3,79	2,89	2,69	2,17	1,67	2,49	2,01	1,81
TXV 2.0t Fujikoki	5,17	3,84	2,47	4,84	4,80	3,97	2,76	2,20	1,75	2,48	2,09	1,78

Additional COP improvement with modified TXV

DuPont — The miracles of science™

Honeywell

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	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

Based on the toxicity results due end of August, 2008, Honeywell and DuPont will be in a position to commit to production of HFO-1234yf

- Second Species Developmental Preliminary Results
  - Based on what we know today, we believe HFO-1234yf will have a no effect level (NOEL) of 4000 ppm. Therefore, we believe HFO-1234yf will not be classified as a developmental toxin in Europe and will be classified as ASHRAE Class A (low toxicity)
  - Final report due end of August, 2008

- Reproductive study is in progress
  - Preliminary Interim results 1-Gen end of August 2008
  - 2-Gen is being conducted to satisfy possible future requests of data

Acute Toxicity Exposure Limit

- It provides an estimate of the maximum exposure limit for a short time period (≤30 minutes) with no adverse health effects.
- HFO-1234yf developmental test results have no impact on ATEL value.

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 – Short Term Tox Exposure Not an Issue for Collisions, Accidental Releases

The Acute Toxicity Exposure Limit (ATEL) is a value used by Standards organizations (e.g., ASHRAE 34, ISO 817) to establish the maximum refrigerant concentration limit for a refrigerant in air. It is calculated from the acute toxicity data using methods determined in accordance with the Standards.

DUPONT The miracles of science™

Excellent Environmental Properties

Honeywell

- **ODP = 0**
- **100 Year GWP = 4** (GWP_{134a} = 1430)
  - 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**

Available online at www.sciencedirect.com
ScienceDirect
Chemical Physics Letters 439 (2007) 18–22
ELSEVIER
CHEMICAL PHYSICS LETTERS
www.elsevier.com/locate/cplett

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

Received 31 January 2007; in final form 6 March 2007
Available online 21 March 2007

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).

0009-2614/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2007.03.053

HFO-1234yf Environmental Properties Have Been Confirmed in an Independent, Peer Reviewed and Published Scientific Paper

Breakdown Product Discussion – Trifluoroacetic Acid (TFA)

- **R-134a breakdown product trifluoroacetic acid (TFA) does not pose a threat to the environment, based on thorough industry evaluations in 1990s**
  - **HFO-1234yf will also breakdown to form TFA**

- **There is a very large quantity of TFA in the sea (Ref: 1, 2, 3); The amount suggests that TFA is a natural component of seawater (3).**
  - **1.** Scott B.F., et al., Haloacetic Acids in the Freshwater and Marine Environment, First International Symposium on Atmospheric Reactive Substances, 14-16 April 1999, Bayreuth, Germany.
  - **2.**Von Sydow L., A. Grimvall, H. Boren, K. Laniewski, A. Nielsen, Natural background levels of trifluoroacetate in rain and snow, Environ. Sci. Technol., 34, 3115-3118, 2000.
  - **3**. Frank H., E.H. Christoph, O. Holm-Hansen and J.L. Bullister, Trifluoroacetate in Ocean Waters, Environ. Sci. Technol., 36, 12-15, 2002.

- **"Based on available data, one can conclude that the environmental levels of TFA, resulting from the breakdown of alternative fluorocarbons do not pose a threat to the environment".**
  - Boutonnet et al., Environmental Risk Assessment of Trifluoroacetic Acid, Human and Ecological Risk Assessment, 5(1), 59-124, 1999.

DUPONT
The miracles of science™

Honeywell

Water Solubility Results

	Water in Refrigerant at 25℃ (ppm)	Water in Refrigerant at 50℃ (ppm)
R-134a	**1000**	**1850**
HFO-1234yf	**320**	**810**

ARI-700, SAE-J2776 Refrigerant Standard for Moisture: 20 ppm max

No water solubility issues expected for HFO-1234yf

HFO-1234yf Desiccant Selection

- Required Desiccant Amount/type Depends on:
  - Refrigerant solubility and reactivity with water
  - Rate of water permeation into a system
  - OEM desired level of system dryness
- R-134a Desiccant
  - Currently use XH-7 or XH-9
  - 40-60 grams typical usage for average R-134a system
- HFO-1234yf Desiccant Testing
  - XH7 and XH9 performed well in HFO-1234yf testing.
  - HFO-1234yf is less reactive with the adsorbent than R134a.
  - Tests were run for 14 days at 82℃ with R134a as a baseline.
  - UOP would recommend starting with the same amount used in today's R134a systems

HFO-1234yf is usable with the same desiccants and amount as R-134a

Electrical Properties

	R-134a	HFO-1234yf
Liquid Dielectric Constant @ 21.3°C	**9.8 (1), 9.0 (2), 9.2 (3)**	**7.7 (1)**
Resistivity, MOhms.m	**9.6(1) 7.3 (2)**	**3.4 (1)**

Data References:

1. Honeywell measurements
2. A. Sekiya & S. Misaki, Journal of Fluorine Chemistry; 101 (2000) pp 215-221
3. C. Meurer, G. Pietsch & M. Haacke, International Journal of Refrigeration, 24 (2001) pp 171-175

HFO-1234yf electrical properties similar to R-134a

HFO-1234yf Will Be Handled Similar to R-134a

- Distribution of HFO-1234yf from manufacturer to auto OEM plants and after sales service markets will be similar to R-134a
- Minor changes to plant charging equipment and procedures
- HFO-1234yf can be recovered, recycled and reused on site at service shops
- HFO-1234yf leaks can be detected with same equipment as R-134a
- Unique fittings will be used ensure no cross contamination with R-134a

Supply Chain Analysis

TÜV Study Description Details

Description of Supply chain

- Substance will be imported in bulk: 15 – 20 MT ISO tanks.
- Storage of Substance in bulk in Port Area

Step 1:

- Substance is shipped from Port to OEM for delivery in Bulk Storage tank (capacity up to 50 MT
- OEM has dedicated filling lines to manufacturing operations, where AC system is charged
- Car is supplied to Distributor, Dealer and customer

Step 2:

- Substance is transferred from Port to Re-packaging site
- Substance is filled in cylinders
- Cylinders are supplied to OEM, then option1

Step 3:

- Substance is transferred from Port to Re-packaging site
- Substance is filled in cylinders
- Substance is supplied to distributor
- Distributor supplies to service centre
- Service centre charges product to Car AC

Step 4:

- Substance is recovered at service point
- Substance is treated in recovery unit or
- Substance must be returned to distributor or waste treatment

Path Forward

• Plant Process Design & Planning	In progress
✓Second Species Development test – Preliminary results	Mar 2008
• Development Test - final report	Aug 2008
• Regulatory: SNAP/ASHRAE filed; REACH to be filed	Jul 2008
• 1-Gen Reproductive test results	Aug 2008
• Obtain Industry convergence/multiple OEM commitments	Sept 2008
•Industry adoption of HFO-1234yf	
•Firm volumes projections to finalize facility plans (June 2008)	
• Obtain Honeywell/DuPont Capital Commitment/Funding	Oct 2008
• Plant Construction end & plant start-up	Nov 2010

The miracles of science™

Honeywell

For further information on HFO-1234yf please visit:

www.genetron.com ,

www.refrigerants.dupont.com , and

www.SmartAutoAc.com

Thank you!