MRB CRP Updated Risk Assessment for Low GWP Blend Refrigerants

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Prior Risk Assessments for Auto AC Systems

- Jetter et al., 2001
  - Generic “proof of concept” paper
- Blackwell et al. (2005, 2006)
  - R-152a and CO₂
- Delphi and Delphi/TUV
  - R-152a
- SAE CRP150
  - 3 new R-134a alternatives (all later withdrawn)
- SAE CRP1234
  - HFO-1234yf and CO₂
- MRB CRP
  - new refrigerant blends
Risk Assessment Approach

Goals
- To determine whether use of new refrigerants increases risks for passengers, service personnel or others relative to existing risks of R-134a
- To assist US EPA in making a SNAP determination

Key Questions
- Effects on health (refrigerant toxicity)
  - Question: How likely is it that there will be an exposure above a health-based limit (HBL)?
- Flammability
  - Question: How likely is it that the refrigerant will be ignited with someone present by foreseeable energy sources or under feasible conditions?
- Decomposition Products
  - Question: How likely is exposure to decomposition products (e.g., HF) in the event of refrigerant ignition or thermal decomposition?
Risk Assessment Approach (cont)

- Scenarios Considered
  - Vehicle Occupants
    - Release from a fault during operation (corrosion, hose leaks)
      - In cabin and in engine compartment (aspiration)
    - Release due to a vehicle collision
      - In cabin and in engine compartment (aspiration)
  - “Good Samaritans”
  - “Bystanders” outside vehicle
  - First responders
  - Repair workers (Professional and DIY)
  - Assembly plant workers
  - Some were addressed qualitatively
Data Collection

- OEM data on vehicle operation
- Literature data on events and behaviors
- Toxicity
  - All components already well tested, evaluated
  - Low acute toxicity for blends, comparable/better than R-134a
- Flammability
  - Basic properties (LFL, UFL, Ign. Temp, burning velocity)
  - Concentration measurement in simulated releases
  - Potential ignition sources
- Decomposition products
  - Bench scale testing
  - Field testing

Focus since summer 2011
Fault Tree Analysis (FTA)

- Similar to EPA sponsored risk assessment of R-152a and R-744 and similar to prior SAE CRP1234
- Results are compared to other non-AC related automotive risks
- Relative to prior SAE effort, added hybrid vehicles and dual evaporator vehicles to evaluation
- Fault trees presented previously were updated to reflect newer information
# Hazard Scenarios Studied in FTA

<table>
<thead>
<tr>
<th>Event Type</th>
<th>Location and Source of Refrigerant Release</th>
<th>Location of Exposed Individual</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Vehicle collisions</strong></td>
<td>- Cabin, Evaporator leak</td>
<td>- Occupant in passenger cabin</td>
</tr>
<tr>
<td></td>
<td>- Engine comp., Broken tube/hose</td>
<td>- Former occupant in engine comp.</td>
</tr>
<tr>
<td></td>
<td>- Engine comp., Broken tube/hose</td>
<td>- Good Samaritan in engine comp.</td>
</tr>
<tr>
<td></td>
<td>- Engine comp., Broken tube/hose</td>
<td>- Occupant trapped in passenger cabin</td>
</tr>
<tr>
<td><strong>Vehicle fires (vehicle in operation)</strong></td>
<td>- Engine comp., Fire damage to AC lines</td>
<td>- Former occupant in engine comp.</td>
</tr>
<tr>
<td></td>
<td>- Engine comp., Fire damage to AC lines</td>
<td>- Occupant trapped in passenger cabin</td>
</tr>
<tr>
<td><strong>Vehicle fires (vehicle parked)</strong></td>
<td>- Engine comp., Fire damage to AC lines</td>
<td>- Vehicle owner/other person in engine comp.</td>
</tr>
<tr>
<td><strong>AC system leaks</strong></td>
<td>- Engine comp., Broken tube/hose</td>
<td>- Occupant trapped in passenger cabin</td>
</tr>
<tr>
<td></td>
<td>- Engine comp., Broken tube/hose</td>
<td>- Former occupant in engine comp.</td>
</tr>
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</table>
Risks Require a Combination of Factors

Top Event
(e.g., Risk of refrigerant ignition)

1. Frequency of initiating event (e.g., collision or hose failure)
2. Probability refrigerant reaches flammable concentration range
3. Probability sufficient ignition source present
4. Modifying factors

All contributing events must align for the top event to occur

1. Data from on modeling and measurement studies, engine compartment geometries
2. Is a hot enough or energetic source likely to present when a release occurs?
3. Vehicle integrity, blower status, timing and location of release relative to ignition source(s), behavioral factors
Collision Trees Account for Speed and Impact Location

Speed dependent factors (e.g., related to crash severity)

Similar structure for high and low speed collisions

Similar structure for front and rear impacts
Sources of Input Data for FTA

- Inputs related to vehicle collisions based on averages of national statistics from several countries
- Inputs related to collision consequences (e.g., AC system damage) estimated based on OEM crash data
- Inputs related to refrigerant concentrations and timing derived from results of modeling & measurement studies
- Assumptions concerning refrigerant ignition and decomposition based on field studies
  - Aware of recent Daimler test results; currently exploring how this new information may affect the FTA
- Inputs where data are lacking were derived as expert OEM consensus
- Inputs considered to be highly uncertain were assessed through sensitivity analysis
Service Scenarios Studied in FTA

<table>
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<tr>
<th>Event Type</th>
<th>Location and Source of Refrigerant Release</th>
<th>Location of Exposed Individual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Certified Technician exposure</td>
<td>Engine comp., Broken tube/hose</td>
<td>Technician in engine compartment</td>
</tr>
<tr>
<td>Certified Technician Ignition Event</td>
<td>Leak at Equipment</td>
<td>Technician in engine compartment</td>
</tr>
</tbody>
</table>

- Evaluated risks of a leak during service in a professional shop
  - Based on CFD conducted for prior CRP (now published), refrigerant leaks are only in the flammable range a few cm out from the leak source
  - Service pits are assumed to be covered by existing confined space regulations and were not included in the risk assessment
- DIYers
  - Modeling indicates that flammable concentrations are not obtained in the heel release and are extremely unlikely in the charge kit leak scenario
DIY Concentration Modeling

- Prior CRP work indicated flammable concentration would only be near the leak location in professional repair cases
  - Flammable zone was only a few cm in length near the leak
- New modeling done to assess risks for DIYers in the event of a charge kit leak or from release of can heel
- Worst-case release rate assumptions in both cases (i.e., no ventilation, high leak rate)
- Neither scenario indicated that flammable concentrations would be reached at any time during the release
Charge kit leak

Peak concentration in plume remains well below LFL (and also the ATEL)

Can heel release

Maximum extent of release above 10% of LFL
FTA Results
<table>
<thead>
<tr>
<th>Event</th>
<th>Probability per vehicle per operating hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Probability of being in a police reported vehicle collision</td>
<td>$5 \times 10^{-5}$</td>
</tr>
<tr>
<td>Probability of vehicle collision due to vehicle brake failure</td>
<td>$3 \times 10^{-7}$</td>
</tr>
<tr>
<td>Probability of highway vehicle fire (any cause)</td>
<td>$1 \times 10^{-7}$</td>
</tr>
<tr>
<td>Probability of an airbag-related fatality associated with a vehicle collision</td>
<td>$2 \times 10^{-10}$</td>
</tr>
<tr>
<td>Probability of vehicle occupant/former occupant experiencing HF exposure above health based limits associated with R-1234yf ignition/decomposition.</td>
<td>$2 \times 10^{-14}$</td>
</tr>
<tr>
<td>Probability of vehicle occupant/former occupant experiencing HF exposure above health based limits associated with AC6 ignition/decomposition.</td>
<td>$1 \times 10^{-14}$</td>
</tr>
<tr>
<td>Probability of vehicle occupant being exposed to an open flame due to R-1234yf ignition</td>
<td>$4 \times 10^{-15}$</td>
</tr>
<tr>
<td>Probability of vehicle occupant being exposed to an open flame due to AC6 ignition</td>
<td>$5 \times 10^{-17}$</td>
</tr>
</tbody>
</table>
## Risk Comparison to Other Workplace Events

<table>
<thead>
<tr>
<th>Event</th>
<th>Probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-fatal recordable Injury at work (all occupations, per working hour)</td>
<td>$2 \times 10^{-5}$</td>
</tr>
<tr>
<td>Probability an AC service technician is struck by object resulting in lost work days (per working hour)</td>
<td>$2 \times 10^{-6}$</td>
</tr>
<tr>
<td>Probability of a fatal fall at the workplace (all occupations, per working hour)</td>
<td>$2 \times 10^{-9}$</td>
</tr>
<tr>
<td>Probability of AC service technician exposure to an open flame due to R-1234yf ignition (per hour of vehicle service)</td>
<td>$8 \times 10^{-21}$</td>
</tr>
<tr>
<td>Probability of AC service technician exposure to an open flame due to AC6 ignition (per hour of vehicle service)</td>
<td>$5 \times 10^{-22}$</td>
</tr>
<tr>
<td>DIYer exposures to AC6 or R-1234yf (per working hour)</td>
<td>Essentially zero</td>
</tr>
</tbody>
</table>
Relative Risk Contribution in FTA

Probability of vehicle occupant being exposed to an open flame due to refrigerant ignition

Combined risk = $4 \times 10^{-15}$

IG1 – collision related release in cabin
IG2 – collision-related release in engine comp.
IG3 – AC system leak in engine comp.

Combined risk = $5 \times 10^{-17}$

Risk for all three refrigerants is dominated by Fault Tree IG1, the scenario involving a collision-related evaporator leak into the cabin.
Relative Risk Contribution in FTA

Probability of vehicle occupant/former occupant experiencing HF exposure above health based limits associated with refrigerant ignition/decomposition

Combined risk = $2 \times 10^{-14}$

HF1 - collision related release into cabin resulting in HF generation
HF7 - non-AC related fire generating HF in engine comp
HF8 – non-AC related fire generating HF which is aspirated into cabin

Risk is dominated by scenarios involving a collision causing an refrigerant release in the cabin (HF1) and a non-AC related vehicle fire (HF7).
Supply Chain Issues

- Risks for automotive workers
  - Charging AC systems in assembly plants
  - General assembly plant workers

- Factors to consider
  - Low toxicity, both acute and chronic, OELs comparable to or higher than other chemicals already in use
  - Flammability is key risk (decomposition in absence of ignition is very unlikely)

- Studies of R134a conducted both at GM and Volvo have indicated very low concentrations in vehicle assembly plants
  - GM measurements (personal and area samplers) show concentrations < 10 ppm
  - Volvo measurements (area samplers) indicated concentrations ≤0.1 ppm
  - The R134a results should be applicable for AC5 or AC6
  - Far below the relevant OELs or LFLs

- Risks for chemical manufacturing workers will be managed by their own internal Health & Safety programs
Comparison of Proposed Substitutes for SNAP

- Key criterion is relative *overall* risk compared to R-12 and R-134a. Overall risk can not be increased

<table>
<thead>
<tr>
<th>Property</th>
<th>R-12</th>
<th>R-134a</th>
<th>AC6</th>
<th>R-1234yf</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Toxicity</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acute toxicity (LC$_{50}$, ppm)</td>
<td>600,000</td>
<td>&gt;500,000</td>
<td>&gt;207,000</td>
<td>&gt;405,000</td>
</tr>
<tr>
<td>Anesthetic potency (ppm)</td>
<td>25,000</td>
<td>50,000</td>
<td>&gt;166,000</td>
<td>120,000</td>
</tr>
<tr>
<td>OEL (ppm)</td>
<td>1,000</td>
<td>1,000</td>
<td>840</td>
<td>500</td>
</tr>
<tr>
<td><strong>ASHRAE ATEL</strong></td>
<td>18,000</td>
<td>50,000</td>
<td>57,100</td>
<td>101,000</td>
</tr>
<tr>
<td><strong>Flammability</strong></td>
<td>None</td>
<td>None</td>
<td>None below 50° C</td>
<td>weakly flammable</td>
</tr>
<tr>
<td>ODP</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>100 year GWP (CO$_{2}$=1)</td>
<td>10,600</td>
<td>1,430</td>
<td>130</td>
<td>4</td>
</tr>
<tr>
<td>Estimated total lifetime annual refrigerant loss rate (grams/year)</td>
<td>--</td>
<td>38</td>
<td>46</td>
<td>38</td>
</tr>
</tbody>
</table>
Overall Risk Assessment Conclusions

- Use of AC6 in MAC systems poses an extremely low level of risk for vehicle operators and repair workers
  - The risks are lower than those estimated for R-1234yf
  - A key risk driver involves HF exposure from a non-AC related fire, a risk that is present with current R-134a systems

- Based on Risk Assessment to date, AC6 could be an appropriate alternative for R134a and R12 as MAC refrigerants
  - Increased risk due to flammability is very small
  - Hazard due to toxicity is equivalent or reduced
  - Environmental benefits (i.e., GWP, ODP, LCCP) are enhanced as compared to R-134a and R-12
Thanks for your attention!