`DEVELOPMENT AND EVALUATION OF AC5 AND AC6 REFRIGERANTS FOR MAC APPLICATIONS

A White Paper produced by the SAE MRB Cooperative Research Programme

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Introduction

The introduction of the European MAC Directive has required the automotive industry and chemical companies to work together to develop alternative refrigerants with GWP of less than 150 to replace R-134a. The first globally agreed candidate alternative fluid, the hydrofluoro-olefin (HFO) R-1234yf, is now entering production and use after an extensive cooperative research programme (CRP-1234) administered by the SAE International and involving global car OEMs and chemical suppliers.

A second SAE-administered CRP (MAC Refrigerant Blend Cooperative Research Program, MRB CRP), involving global OEMs and Tier One air conditioning system suppliers, has been working since early 2011 to evaluate the potential adoption for MAC application of two low-GWP, zeotropic refrigerants originally developed by Mexichem Fluor as medium low pressure fluids having similar operating pressures to R-134a. These fluids, AC5 (now designated R-444A by ASHRAE) and AC6 (provisionally designated R-445A by ASHRAE) are both based on the HFO R-1234ze(E). This White Paper presents a summary of the work done so far by the CRP in evaluation of these fluids.

The project has been operated in three phases. The first phase, ran from February to October 2011, and a basic feasibility assessment of both fluids was carried out during this time. The testing methodology was developed from the framework of the previous CRP-1234 and the same outside laboratories were used. However since some of the information and analysis of that project was not publicly available, certain areas of work – notably the development of a fault tree analysis – had to be developed from first principles by the team members. In addition to the scope of investigation covered by the CRP-1234 activities it was also agreed to extend the safety and risk assessment to car systems having a dual (rear) evaporator and to electric or hybrid vehicles.

The reason for evaluation of two fluids in parallel were simple: both fluids offered some attractive features to the OEM members of the CRP team, and it was felt that the best way to proceed was to assess both using similar methodologies and evaluation criteria.

Both fluids studied in this project are ternary refrigerant mixtures. AC5 is a formulation of R-32/R-152a/R-1234ze(E) in the nominal proportions (by weight) 12%/5%/83%. AC6 is a formulation of R-744, R-134a and R-1234ze(E) in the nominal proportions 6%/9%/85%. AC5 was formulated to give a close performance match to R-134a whilst having similar flammability characteristics to R-1234yf. AC6 was formuated to give a fluid having somewhat higher refrigeration capacity than R-134a (originally for a stationary refrigeration application) but with reduced flammability compared to R-1234yf. In fact, AC6 is not flammable at normal ambient temperature, whereas both R-1234yf and AC5 are flammable at ambient temperature.

They are both zeotropic mixtures, meaning that they exhibit a difference in compositions between liquid and vapour at equilibrium, and undergo a temperature change [often referred to as temperature glide] during evaporation or condensation. The implications of these characteristics for the project activities were considerable:

- Performance testing was carried out to assess the effect of composition change on cooling capacity and energy efficiency as well as an assessment of the impact of temperature glide in the evaporator and condenser
- Assessment was needed of the potential for composition changes in a car a/c system during service activities, with identification and demonstration of methods for enabling onsite recovery of the refrigerant and recharge of MAC systems with the correct refrigerant composition
- The best method to fill vehicles on assembly lines had to be identified and field tested
- Leakage testing on systems and hose permeation testing had to take account of and measure the potential for the constituents of the refrigerant mixture to leak at different rates.
- In flammability assessment a range of possible compositions were tested to ensure that the worst case composition was identified and its flammability characteristics were properly understood
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Subsequent sections of this document provides more detail on these points.

The first phase of the project was completed in September 2011 and in this period the team covered most of the equivalent scope carried out by CRP-1234, but for two fluids and in a period of 9 months rather than two years. At the end of phase one both fluids seemed to be acceptable on the basis of the initial flammability, materials compatibility and performance tests. In particular it was found that the hot metal surface temperature required to ignite a spray of either fluid mixed with PAG lubricant was about 100K higher than that required to ignite a R-1234yf/lubricant spray, with other flammability characteristics such as ignition energy found comparable or more favourable than those of R-1234yf.

The second phase of the project ran from October 2011 to October 2012. In this phase more team members joined. The focus was switched to more in-depth assessment of remaining key technical issues likely to be found in using and handling zeotropic refrigerants: a more detailed study of ignition source and underhood flammability; study of potential for selective leakage to alter refrigerant composition, investigation of different heat exchanger designs for use with AC6, and longer term testing of compressor durability. The fault tree analysis was also continued and extended as more data was generated by the programme activities.

The conclusion of Phase 2 activities was that both fluids could be candidate alternatives to R-134a or R-1234yf for MAC application, with acceptable safety and environmental performance. It was agreed in October 2012 that a final phase of the project should be carried out, focusing on the AC6 fluid as it had demonstrably lower risks associated with its flammability but also required some further effort in addressing questions around composition maintenance in car and during service.

In the third and final ongoing phase of the project, which is scheduled to finish in October 2013, the goals of the programme are: to enable the construction and demonstration of prototype equipment for handling the refrigerant; to review and consolidate understanding of the flammability characteristics of AC6 in real world scenarios (such as potential for ignition in engine compartments); to develop recommendations for working standards on the use of the refrigerant in MAC applications; to produce supporting information to enable SNAP submission of the fluid, and to demonstrate engineering approaches to further improve performance by modifying system design to allow for the zeotropic fluid characteristics.

Physical Properties

The main thermophysical properties of the fluids are summarised in Table 1. Both AC5 and AC6 have molecular weight, liquid density, latent heat of vaporisation and critical points that are close to those of R-134a. This is by design as the fluids were formulated to give operating pressures and cooling capacities close to those typically found using R-134a.

	R-134a	**R-1234yf**	**R-444A (AC5)**	**R-445A (AC6)**
Molecular weight (g/mol)	102.03	114.04	96.70	103.1
Global Warming Potential[1]	1430	4	92	130
Critical Temperature (°C)	101.1	94.7	103.2	98.0
Critical Pressure (kPa)	4059	3382	4278	3973
Normal boiling point/range (°C)	-26.1	-29.4	-34.3 to -23.3	-48.3 to -21.5
Liquid density at 25°C (kg/m^3)	1206	1092	1140	1133
Latent heat of vaporisation at atmospheric pressure (kJ/kg)	217	145	184	236

Table 1: main physical properties of the refrigerants

A physical property model for these refrigerants has been developed by Mexichem Fluor, using the short-form Span-Wagner (Helmholtz free energy) equation of state implemented in NIST's REFPROP™ software (v8.0 or higher). The model was developed in conjunction with the Laboratory for Thermophysical Properties at the Technical University of Oldenburg, Germany. The liquid and vapour densities and heat capacities of R-1234ze(E) were measured experimentally then combined with measurements of vapour pressure and critical point, and ideal gas enthalpy derived from molecular mechanics simulation, to give an accurate equation of state for R-1234ze(E). The vapour liquid equilibrium between mixtures of R-1234ze(E) and each of the other fluid components was then studied and used to derive binary interaction parameters for incorporation to the model, allowing estimation of ternary mixture properties.
The liquid thermal conductivity, liquid surface tension and liquid and (low pressure) vapour viscosity of pure R-1234ze(E) refrigerant were also measured and found to be close to the properties of R-134a.

The physical property model for the fluids is available as a set of files compatible with REFPROP 8.0 or higher from Mexichem Fluor.

[1] Calculated using IPCC AR4 values for the HFC components and a value of 6 for the GWP of R-1234ze(E)

Solubility, Miscibility, lubricity of several oil/refrigerant mixtures have also been measured as part of the CRP.

Lubricant and Material Compatibility Studies

Materials compatibility, miscibility, solubility, tribological effects and electrical properties were studied for the refrigerants and their mixtures with POE and PAG lubricants at the Institut für Luft und Kälte Technik (ILK) in Dresden, Germany. Further studies on refrigerant/lubricant interaction were carried out at Mexichem's laboratory in the UK.
Four different oils were evaluated with a range of different elastomers currently in use in mobile air conditioning systems. The worst case purity of the refrigerant was evaluated with several of these materials. A few materials were found sensitive to some refrigerant and oil combinations but most materials showed acceptable properties after testing.

In general the electrical properties of both refrigerants mixed with oil were found acceptable (and improved relative to R-1234yf). The material compatibility testing showed similar behaviour in overall terms compared to R-1234yf.
Miscibility and solubility of these refrigerants provide properties that are more conducive to compressor durability than R-1234yf. Preliminary durability testing was conducted at ILK as well as at each of the four Tier One suppliers involved in this CRP. While there were no significant issues identified in this testing, more extensive testing will be conducted in the future.

Performance and Environmental Impact

Performance of the fluids has been extensively studied in automotive air conditioning systems using a variety of system configurations, in bench calorimetry and vehicle (wind tunnel) tests. The scope and range of testing is shown in Table 2.

Vehicle system	Test type	Purpose
US OEM #1	System Bench testing	Drop In performance as well as system optimization
US OEM #2	Wind tunnel testing	Cool down performance
Asia OEM #3	Wind tunnel testing	Vehicle level performance, TXV tuning
Asia OEM #4	System Bench testing	Heat Exchanger optimization
Asia OEM #5	System Bench testing	Heat pump development
EU OEM #1	Wind tunnel testing	Cool down performance
EU OEM #2	System bench testing	Drop in testing and system optimization
EU OEM #3	Wind Tunnel testing	Cool-down performance
EU OEM #4	Wind Tunnel testing	Cool-down performance and system optimization

Table 2: performance testing studies

The scope of testing has included “drop-in” testing on systems designed for R-134a and R-1234yf, and some soft optimisation studies including superheat/subcooling studies, installation of internal suction/liquid heat exchangers, and compressor displacement optimisation. Alternate configurations of condenser (varying pass configuration, and assessment of cross-counterflow geometry) and evaporator (varying pass configuration, including cross-counterflow geometry) have been assessed to determine which may be best suited for use with AC6 and its associated temperature glide.

Wind tunnel and bench testing was also used to determine the minimum acceptable level of R-744 in the refrigerant to maintain acceptable cooling performance at high load. This was found to be about 4% R-744. Full testing according to the SAE test matrix [SAE J2765] for life-cycle climate performance evaluation was carried out for both AC5, AC6, R-134a and R-1234yf in a reference system to allow evaluation of environmental impact of the fluids in MAC application.

The main findings can be summarised as follows:

- Drop-in performance of AC5 shows performance similar to R-134a at most test conditions, with capacity and COP close to R-134a values
- Drop-in performance of AC6 shows performance similar to R-134a at high load (high ambient/high compressor speed) conditions with a loss COP of the order of 5-10% at part load conditions. This is accompanied by an increase in discharge pressure, which is possibly partially attributed to a tendency for the refrigerant to liquid-fill the condenser.
- By the selection of an appropriately sized internal heat exchanger and separated receiver dryer components it is possible to achieve improved AC6 performance (relative to R-134a) at part load conditions and overall equivalent or improved performance relative to R-1234yf in the same system

Figure A shows performance during pulldown in one of the systems tested

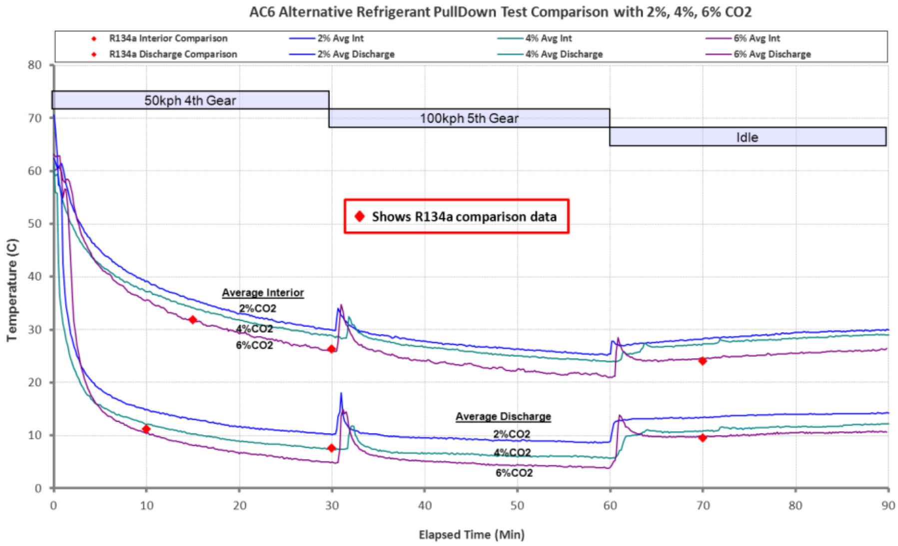

Figure A: pulldown curves for varying composition of AC6

LCCP analysis using the GREEN-MAC software tool showed that the overall LCCP of both AC5 and AC6 derived from this reference system is similar or better than that of R-1234yf and significantly improved compared to R-134a. Figure B shows the output from the LCCP analysis for major US regions.

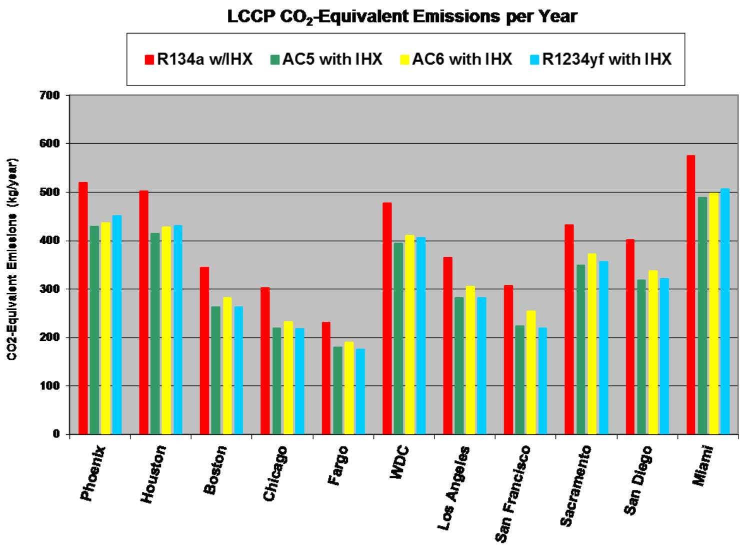

Figure B: LCCP estimates for R-134a and low GWP fluids

Work is ongoing to improve understanding of how to further improve the performance of AC6 at part-load conditions, including studies on charge determination method, exchanger pass configuration and refrigerant flow distribution.

Zeotropic effects in handling and use

As previously mentioned both AC5 and AC6 are zeotropic refrigerant mixtures. AC6 is made up of R-744/134a/1234ze(E) (6.0/9.0/85.0) with tolerances of (±1.0/±1.0/±2.0). AC5 is made up of R-32/152a/1234ze(E) (12.0/5.0/83.0) with tolerances of

(±1.0, ±1.0, ±2.0). The consequences of this for handling and servicing are as follows:

- There is a composition difference present between liquid and vapour when a system is at rest or the refrigerant is stored in a cylinder. The vapour is enriched in the more volatile species: R-32 in the case of AC5; R-744 in the case of AC6.
- The degree of difference in the phase compositions depends on the temperature and also the relative proportions of the volume occupied by liquid and vapour phases.
- If a cylinder or tank is depleted of refrigerant by removing liquid, the proportion of volatile component remaining in the liquid drops. For AC5 this effect is not significant – the change in R-32 content between that of a liquid filled cylinder and a practically empty cylinder is within the production tolerance. For AC6 on the other hand this volumetric effect would result in the liquid content moving outside its R-744 specification after removal of about 80% of the cylinder contents.

These composition difference effects in handling and filling have been investigated by practical (experimental) tests and by computer simulation. The refrigerant property model has been found to give a good representation of the compositional difference between liquid and vapour for both refrigerants. This has been verified by carrying out experimental testing of vapour removal from a cylinder with periodic GC analysis of the vapour composition, then comparing the results from those predicted by modelling the vapour leak.

<u>Service and recovery testing</u>

The effect of service and handling of AC5 and AC6 on refrigerant composition was studied by testing repeated charging and recovery of a car a/c system using commercially available equipment designed for R-1234yf recovery.

In this work a car was repeatedly charged with material from a single cylinder, originally filled to the correct composition. The car was acclimatised in a climate chamber prior to each charging operation. After charging, the car was run for a period of time then the material was recovered into a recovery cylinder. Composition samples were taken throughout each test as follows:

- Pre-charge – direct from charging cylinder
- Engine & compressor running – direct from High and Low service port fittings
- Engine and compressor off – direct from High and Low service port fittings
- Recovered state – direct from recovered one litre cylinders

It was found that the typical handling and recovery procedures employed today with R134a in an automotive workshop could affect the composition of both fluids but that the effect was more significant for AC6 than for AC5. The composition of AC5 was largely preserved within acceptable specification limits whereas the composition of AC6 was reduced in R-744 after recovery.

In this case the R-744 component concentration would typically be reduced from its nominal value of 6% and the extent of the reduction varied in a (predictable) manner depending on system volume and ambient temperature. It was also found that routine handling operations did not significantly alter the ratio of R-134a to R-1234ze(E) in the refrigerant. This suggested that the best way to handle AC6 in a recovery scenario would be to check the composition of recovered refrigerant and to add R-744 as needed to the material on its recharge to the car.

It was also identified that when the engine was running the refrigerant composition in circulation rapidly returned to the expected composition,

Figure C shows a summary of measurements taken on R-744 composition by way of illustration of the findings.

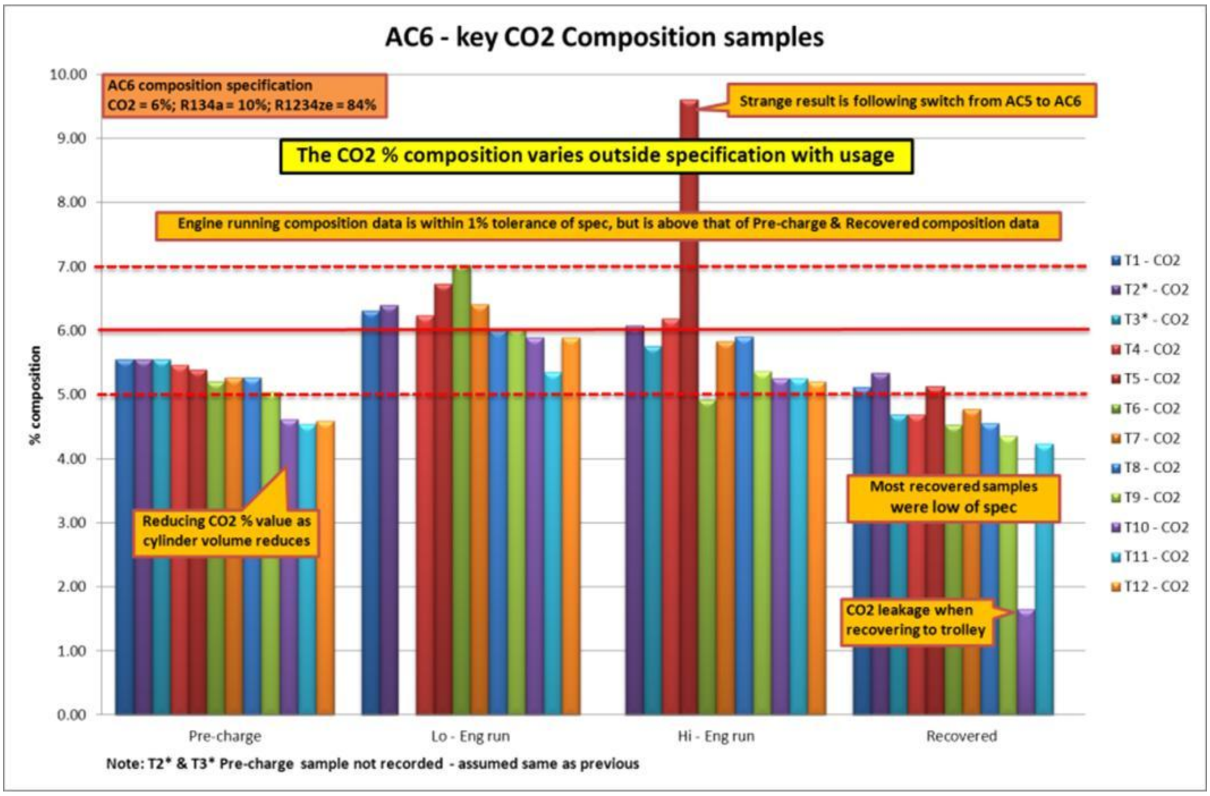

Figure C: summary of AC6 charging tests on R-744 composition

Work is now ongoing to adapt service equipment to allow automated correction of the R-744 content before return of recovered refrigerant to a vehicle system. The modified recovery quipment is being designed so that the operation of the equipment from the technician's perspective will be essentially unchanged from handling a single component refrigerant and that the fluid composition will be brought back to the target value of R-744 with better accuracy than is required by the ASHRAE compositional tolerance. The onboard refrigerant identifier already incorporated in today's designs for R-1234yf recovery units will be used to check R-744 content and appropriate automated adjustment of composition will take place prior to vehicle recharge.

First fill of systems in factories

Work is on-going to develop a robust process for charging the refrigerant into a vehicle in the vehicle assembly process. It has been found by experiment that the best way to achieve correct composition in the shortest possible cycle time is to mix a binary mixture of R-134a and R-1234ze(E) with R-744 in a small receiver vessel. This also has the benefit of simplifying logistics of refrigerant shipment, as it means bulk movement of the binary mixture and R-744, rather than bulk movement of ternary blend, which could lead to changes in the ternary composition through the supply chain.

Protoype filling equipment has been constructed by one of the project members and succesful validation of the filling cycle within an acceptable timescale is on-going. The results of the filling tests will be validated by GC analysis of the material prior to introduction to the system and once filled into the system. Further demonstration by filling into a range of vehicle types together with optimisation of the cycle time is planned for the coming months.

Leakage from systems

Leakage of both AC5 and AC6 by permeation through hoses has been studied at ILK Dresden using two apparatus designs. The first apparatus design was a standardised single-hose assembly, with the hose section being charged with a fixed mass of refrigerant/lubricant mixture,sealed and heated to 90C in an enclosed apparatus. A sweep of inert gas through the apparatus was then analysed for presence of the refrigerant components and the variation of concentration over time was then used to estimate leakage rates.

A range of production MAC hoses were tested in this apparatus. The best performing hoses were then tested again in a modified apparatus. The modified apparatus consisted of a small sample cylinder holding liquid refrigerant connected to a hose section. The purpose of this was to ensure that the vapour composition remained constant during the course of the leakage study. These tests were run in a temperature range of 30-90°C to allow better estimation of the leak rates that could be expected at the more typical temperature/pressure conditions.

Additional system level testing has been conducted at Creative Thermal Solutions to evaluate some of the more promising hose alternatives. Together with this, a model of leakage over time from a typical system has been developed based on typical ambient temperature profiles and with typical hoses today, the R-744 concentration can be maintained above 4% for 4-6 years. The possibility of evaluating further improved hoses is being discussed with a hose supplier in phase III.

Flammability and Risk Assessment

A detailed quantified risk assessment using Fault Tree Analysis methodology has been developed using an external expert to compare the risks of use of the new fluids with R-1234yf and R-134a. The methodology used was based on that used in the CRP1234 assessment of R-1234yf, however, this analysis also included assessment of single and dual evaporator systems and of electric vehicles. The work completed at the end of 2012 showed that for AC6 the worst case risks were reduced compared to R-1234yf, with up to two orders of magnitude reduction. AC5 was found to be comparable to R-1234yf in overall risk profile. The analysis is summarised in Table 2. This analysis is being reviewed as part of the ongoing project activities. An independent third party expert body has been engaged to provide a critical review of the final fault tree to assure the team that it is rigorous and conservative.

Event	**Probability/Risk** **(per vehicle per operating hour)**
Being in a police reported vehicle collision	$5x10^{-5}$
Vehicle collision due to vehicle brake failure	$3x10^{-7}$
Highway vehicle fire (any cause)	$1x10^{-7}$
An airbag-related fatality associated with a vehicle collision	$2x10^{-10}$
Vehicle occupant/former occupant experiencing HF exposure above health based limits associated with AC5 ignition/decomposition.	$4x10^{-14}$
Vehicle occupant/former occupant experiencing HF exposure above health based limits associated with R-1234yf ignition/decomposition.	$2x10^{-14}$
Vehicle occupant being exposed to an open flame due to AC5 ignition	$2x10^{-14}$
Vehicle occupant/former occupant experiencing HF exposure above health based limits associated with AC6 ignition/decomposition	$1x10^{-14}$
Vehicle occupant being exposed to an open flame due to R-1234yf ignition	$4x10^{-15}$
Vehicle occupant being exposed to an open flame due to AC6 ignition	$5x10^{-17}$

Table 3: summary of fault tree analysis findings

A broad range of flammability studies has been undertaken for both refrigerant blends, with comparative testing to R-134a and/or R-1234yf as part of the work. The scope of flammability assessment has included:

- Flammable limit investigation using ASHRAE Std 34 methodology [LFL and UFL]
- Gas auto-ignition temperature using ASTM E659-78
- Minimum ignition energy testing using ASTM 681
- Burning Velocity
- Heat of Combustion
- Quenching Distance
- Hot surface exposure testing in customised “hot box” testing
- Vehicle testing with hot surfaces located in the under bonnet area
- Ignition source evaluation using automotive components

Endpoint	AC6	R-152a	R-1234yf	AC5	R-134a
LFL (% volume in air)	None at ambient temperature, 8% at 60°C	3.9	6.2	8	NA
UFL (% volume in air)	None at ambient temperature, 12% at 60°C	16.9	12.3	13	NA
Minimum Ignition Energy (mJ)	>5,760	0.38	6250	2250	NA
Hot surface ignition temperature (ºC)	880-960(3)	Not tested	710-810(3)	840-900(3)	Not tested
Heat of combustion (kJ/g)	9.9	16.3	10.7	10.8	
Burning velocity (cm/s)	None	23	1.5	3.9 for WCFF	NA
Quenching distance (mm)	>6	No data	No data	>6	n/a
ASHRAE Safety Classification	A2L	A2	A2L	A2L	A1

(3) From INERIS report #117806, Table 6

The main findings can be summarised:

The flammability characteristics of AC5 are in overall terms similar to R-1234yf although there are some minor differences between them.

In contrast AC6 is less flammable than either fluid; it is non-flammable at normal ambient temperatures, exhibiting flammability onset (by the ASHRAE test method) between 50 and 60°C. Its flammability range is very small with an LFL higher than either of the other fluids.

Like R-1234yf, both AC5 and AC6 are considered to exhibit 2L flammability by the ASHRAE classification method.

In testing of the consequences of spraying refrigerant/oil mixtures onto hot surfaces it was found that a significantly hotter metal surface was required to ignite an aerosol of AC6 with PAG oil. The temperature of metal required was typically 80-100K higher than that needed to ignite R-1234yf/PAG mixtures in the same test. The gas auto-ignition temperature of AC6 refrigerant in its worst case formulation was determined to be about 80K higher than that of R-1234yf in the same apparatus.

The occupational exposure limit(OEL) for AC6 has been calculated as 800 ppm, based on the OELs of its components, and is similar to those of R-1234yf and R-134a.

Ongoing Phase 3 Activities

Summary

Extensive evaluation has been carried out on two zeotropic refrigerants, AC5 (R-444A) and AC6 (R-445A), to ascertain their suitability for application in mobile air conditioning systems. Both refrigerants are promising alternative candidates to R-134a, whose environmental and safety performance has been demonstrated. Risk has been investigated, assessed and judged acceptable for use in mobile air conditioning systems by the CRP team. CRP evaluations are based on the technical evaluation made by the team members.

The research work continues to focus on the AC6 formulation to answer all remaining technical questions, to provide further guidance for how future system development may improve environmental performance and to demonstrate new service equipment for on site MAC system service techniques for handling and servicing systems containing the fluid. The project aims to report final findings at the SAE “TMSS” symposium in Troy, Michigan in October 2013.

Sponsors of the MRB CRP include the following:
Behr, Bosch, Chrysler, Cinetic Filling, Daimler, Denso, Doowon, General Motors, Halla Visteon Climate Control, Hyundai, Jaguar Land Rover, Mexichem, Nissan, PSA, Renault, SAIC Motors, Sanden, Schrader International, TEXA, Volvo Cars