35th International Electric Vehicle Symposium and Exhibition (EVS35)
Oslo, Norway, June 11-15, 2022

Novel Refrigerant Solution for Electric Vehicle Heat Pumps

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Summary

Heat pumps (HP) are being deployed for battery electric vehicles (BEV) to help address deficiencies in thermal management due to the absence of waste heat from traditional combustion engines. Increasing power demands and improved vehicle range is resulting in an evolution where heat pump adoption is essential. The current refrigerant, R-1234yf, has many benefits including ultra-low global warming potential (GWP), but exhibits performance limitations in low ambient temperatures.

The development and performance assessment for a novel refrigerant blend which shows an increase in heating capacity (approximately 25%) and cooling capacity (>20%) while also yielding an improved coefficient of performance (average of approximately 3%) when compared directly to R-1234yf is presented.

Keywords: BEV (battery electric vehicle), Air conditioning, Heat pump, Thermal Management, Vehicle Performance

1 Introduction

Innovations in both design and performance of BEV is challenging existing vehicle thermal management systems which are becoming a top priority for the industry. Vehicle range, cabin comfort, charging speed and assisted driving systems will require a differentiated approach in thermal management. Heat pumps are an attractive prospect as they are an extension of traditional automotive air conditioning (AC) systems and can more effectively manage heat loads for cabin comfort and auxiliary systems. Optimization of the working fluid (i.e. refrigerant) in heat pumps yields a direct vehicle performance improvement while minimizing cost and complexity.

There are trade-offs in optimizing a refrigerant, but providing low global warming potential, class A2L flammability, favorable toxicity, good material compatibility and stability are expectations for a viable working fluid for electric vehicles. Characteristics such as capacity, coefficient of performance (COP), and glide can significantly impact a heat pump system design and therefore must be optimized via fluid selection to both minimize system size and maximize performance. This paper highlights a novel refrigerant solution in comparison to R-1234yf and includes the physical properties, material compatibility, thermal stability, performance modeling, and flammability assessments.

2 Fluid Selection

Presently, no single refrigerant molecule is able to meet all the goals for the evolving EV industry. Tailoring refrigerant blends with R-1234yf, the widely accepted low GWP (values of 4 and 1 based on AR4 [6] and AR5 [7] respectively) molecule in vehicle air conditioning systems today, provides a logical path forward in developing a more desirable working fluid for these heat pump systems. The boiling point and subsequent operating range of R-1234yf in ambient climates below approximately -10°C to -15°C is prohibitive requiring current systems to employ electrical heat in the form of a positive temperature coefficient (PTC) heater. These heaters operate at a COP of 1 or lowr and add both cost and weight to the vehicle. In order to address this operating envelope limitation, R-32 additions to the blend were evaluated. R-32, with a normal boiling point of -51.7°C, can reduce the minimum operating temperature in heating mode and significantly increase the capacity of the refrigerant blend. However, there is a limit to the amount of R-32 that can be practically used as R-32 has a GWP of 675 based on AR4. Another criteria identified for BEVs was impoving the overall system performance and finding a more efficient fluid compared to R-1234yf. R-152a, a refrigerant molecule studied previously in the automotive industry, forms an azeotrope with R-1234yf and has shown to have a positive impact on cycle efficiency. To maintain an A2L safety classification, the maximum R-152a concentration considered was limited to approximately 20 percent by weight in the blend

Table1: Individual Blend Component Properties

Properties	R-1234yf	R-32	R-152a
AR4 100-year GWP	4	675	124
AR5 100-year GWP	1	677	138
Normal Boiling Point (°C)	-29.5	-51.7	-24.0
ASHRAE Standard 34 Safety Classification [2]	A2L	A2L	A2

Discussions with the stakeholders, which includes vehicle OEMs (original equipment manufacturer), AC and HP system facbricators, and component manufacturers, resulted in the development of refrigerant performance criteria for the next generation of thermal management systems. Outside of the fundamental industry expectations for refrigerants which include zero ozone depletion potential, low toxicity, good material compatibility, and good thermal stability, the performance targets are outlined in Table 2.

Table2: Refrigerant Performance Criteria

Criteria	Targets
Volumetric capacity	>20% over R-1234yf
COP	> R-1234yf
Average Glide[1]	< 3K
Safety Classification per ASHRAE 34	A2L
GWP	< 150
NBP	< R-1234yf to maintain positive suction pressures at low ambient heating conditions

[1]Average glide is defined as the average of condenser and evaporator glides over a range of operating conditions

3 Refrigerant Properties

3.1 Thermo-Physical Properties and Thermodynamic Cycle Performance

Using extreme conditions for both AC and HP operations, performance evaluations against R-1234yf were conducted with respect to the noted criteria from the stakeholders. An optimal blend with mass concentrations of 7.5% R-32, 78.0% R-1234yf, and 14.5% R-152a was selected and given the developmental name of HFOG7. Table 3 summarizes key thermo-physical properties of the incumbent fluids (R-134a and R-1234yf) compared to HFOG7.

Table3: Thermo-Physical Properties

Properties	R-134a	R-1234yf	HFOG7
Relative molar mass (g/mole)	102.0	114.0	95.5
Normal Boiling Point (°C)	-26.1	-29.5	-37.3
Dew-point temperature at 101 kPa (°C)	-26.1	-29.5	-32.1
Critical Temperature (°C)	101.1	94.7	94.1
Critical Pressure (kPa)	4059	3382	3956
Specific volume at the critical point (m3/kg)	0.00195	0.00210	0.00224
Latent heat of vaporization @ 60°C (KJ/kg)	139.1	110.4	127.9
Specific heat ratio of the vapor at 60°C	1.45	1.45	1.51
Occupational Exposure Limit (ppm)	1000	500	605
Global Warming Potential (AR5)	1300	<1	72
Safety Class (ASHRAE)	A1	A2L	A2L

Example AC and heating cycle performance can be seen in tables 4 and 5. These evaluations were conducted using Cycle_D version 6.0 software from NIST [5]. HFOG7 results at the AC condition exhibited a 22.6% increase in relative cooling capacity and a 1.0% increase in relative COP whereas heating mode showed a 25.1% increase in relative heating capacity and a 3.7% increase in relative COP when compared directly to R-1234yf.

Table4: Thermodynamic Cycle Performance for AC Condition

Refrigerant	GWP (AR5)	Suction Pressure (kPa)	Discharge Pressure (kPa)	Discharge Temperature (C)	Avg. Glide (K)	Cooling Capacity (kJ/m^3)	COP
1234yf	1	316	1018	54.9	0	1974	3.73
HFOG7	72	372	1223	64.0	3.5	2419	3.77

Evaporator = 0ºC, Condenser = 40ºC, Evaporator superheat = 10ºC, Subcool = 0ºC and Compresor Efficiency =70%

Table5: Thermodynamic Cycle Performance for Heating Condition

Refrigerant	GWP (AR5)	Suction Pressure (kPa)	Discharge Pressure (kPa)	Discharge Temperature (C)	Avg. Glide (K)	Heating Capacity (kJ/m^3)	COP
1234yf	1	99	1302	73.3	0	838	2.19
HFOG7	72	115	1557	90.3	2.75	1049	2.27

Evaporator = -30ºC, Condenser = 50ºC, Evaporator superheat = 10ºC, Subcool = 0ºC and Compresor Efficiency = 70%

3.2 Material Compatibility

HFOG7 was evaluated for compatibility with an array of plastics commonly used in refrigeration and air conditioning applications. Sealed glass tubes [1] were prepared containing HFOG7, POE lubricant (ND-11), and the materials of interest. The tubes were held at 100℃ for two weeks and the materials were removed. Measurements for weight, linear swell, and hardness were recored before and after exposures so differences could be assessed. Two exposure measurements, immediately after exposure (0 hours) and after 24 hours of exposure, were taken to determine if a time dependent recovery effect occurs with polymers or plastics after separation from refrigerant.

Table6: Plastics Compatibility with HFOG7 and ND-11 Oil

Plastics after 0 hrs	0 hr Rating	0 hr % Weight Change	0 hr % Linear Swell	0 hr Hardness Change, Delta
Torlon polymer (polyamide-imide plastic)	0	0	0	-2
Ryton polymer (polyphenylene sulfide)	0	0	0	0
PEEK (Ketaspire 820 NT)	0	0	0	0
nylon 6.6 polymer plastic (Zytel 101)	0	0	0	0
teflon PTFE	0	2	1	-2
nylon resin - Zytel 330	0	0	-10	1
Plastics after 24 hrs	0 hr Rating	0 hr % Weight Change	0 hr % Linear Swell	0 hr Hardness Change, Delta
Torlon polymer (polyamide-imide plastic)	0	-1	0	0
Ryton polymer (polyphenylene sulfide)	0	0	0	0
PEEK (Ketaspire 820 NT)	0	0	0	0
nylon 6.6 polymer plastic (Zytel 101)	0	0	0	1
teflon PTFE	0	2	1	-2
nylon resin - Zytel 330	0	0	-10	1

Rating:
0 < 10% weight gain, and < 10% linear swell and < 10 hardness change
1 > 10% weight gain, or > 10% linear swell or > 10 hardness change
2 > 10% weight gain, and > 10% linear swell and > 10 hardness change

Identical to the plastics compatibility testing, selected elastomers common to AC and HP systems were evaluated for compatibility with HFOG7 and POE oil.

Table7: Elastomers Compatibility with HFOG7 and ND-11 Oil

Plastics after 0 hrs	0 hr Rating	0 hr % Weight Change	0 hr % Linear Swell	0 hr Hardness Change, Delta
Neoprene C1276 -70	0	4	1	-4
Neoprene C0873-70	1	8	3	-10
Epichlorohydrin	1	6	1	-10
Butyl Rubber	1	14	5	-21
EPDM	1	13	4	-13
Fluorosilicone	1	20	7	-20
HNBR	1	16	5	-9
NBR	0	10	2	-9
Fluorocarbon FKM V0747-75	2	25	11	-17
Viton A	2	24	11	-17
Viton GF	2	20	10	-15
Plastics after 24 hrs	0 hr Rating	0 hr % Weight Change	0 hr % Linear Swell	0 hr Hardness Change, Delta
Neoprene C1276 -70	0	2	1	-1
Neoprene C0873-70	0	6	3	-8
Epichlorohydrin	0	4	1	-9
Butyl Rubber	1	13	4	-17
EPDM	1	8	3	-12
Fluorosilicone	1	4	2	-11
HNBR	1	12	4	-7
NBR	0	6	2	-7
Fluorocarbon FKM V0747-75	1	13	6	-15
Viton A	1	14	6	-15
Viton GF	1	10	5	-13

Rating:
0 < 10% weight gain, and < 10% linear swell and < 10 hardness change
1 > 10% weight gain, or > 10% linear swell or > 10 hardness change
2 > 10% weight gain, and > 10% linear swell and > 10 hardness change

3.3 Thermal Stability

Thermal stability was conducted for HFOG7 with lubricant using ASHRAE Standard 97 [1]. The glass tubes were loaded with carbon steel, copper, and aluminium coupons and filled with neat refrigerant and lubricant plus refrigerant. Air and moisture contanimants were added to neat refrigerant and lubricant plus refrigerant mixtures. Tubes were sealed and aged at 175°C for two weeks. Fluoride ion concentration, total acid number and refrigerant purity were measured as an indication of fluid decomposition under the given conditions. HFOG7 stability results were similar to R-1234yf at the same condtions.

Table8: Thermal Stability

Time in Oven	Temp (°C)	Type of Oil	Air (mm Hg)	Water (ppm)	Fluoride Ion (ppm)	Acidity (ppm HCl)	Total Acid Number (mg-KOH/g)	Purity (%)	Visual Observation
2 weeks	175C	no oil	0	0	<MDL[1]	3.4	-	99.9444	Clean coupons, clear and miscible liquid
2 weeks	175C	no oil	76	500	10.6	14.2	-	99.9319	Light tarnish on copper
2 weeks	175C	POE ND-11	0	0	<MDL	-	1.6	99.9446	Clean coupons, clear and miscible liquid
2 weeks	175C	POE ND-11	76	500	<MDL	-	0.4	99.9385	Slightly yellow liquid with some tarnish on coupons

[1]MDL – Minimum detection limit

4 Flammability Assessment

4.1 Burning Velocity & Lower Flammability Limits

The subclass of 2L refrigerants per ASHRAE Standard 34 requires that all of the criteria of Class 2 be met plus the additional requirement that the maximum burning velocity be a value of less than or equal to 10 cm/s when meaured at 23°C and 101.3kPa in dry air. A vertical tube burning velocity apparatus was used in measuring the maximum burning velocities for the refrigerant concentrations of intersest. The apparatus uses a Pyrex tube, 40mm ID by 1.3m long. The flame was observed and recorded from the front and the side using a mirror positioned at a 45-degree angle to the frontal viewing plane. Images of the fully developed flame front were used to measure the frontal area of the flame, from which the burning velocity was calculated. For this blend, both the worst case formulation of flammability or WCF (based on manufacturing tolerances applied to the nominal blend) and the worst case of fractionation for flammability or WCFF (based on leak scenarios) per ASHRAE Standard 34 were evaluated. The WCF for burning velocity was defined as 8.0% R-32, 77.0% R-1234yf, and 15.0% R-152a while the WCFF for burning velocity was defined as 0.1% R-32, 80.4% R-1234yf, and 19.5% R-152a. HFOG7 burning velocity results for the WCF and WCFF are shown in Figure 1.

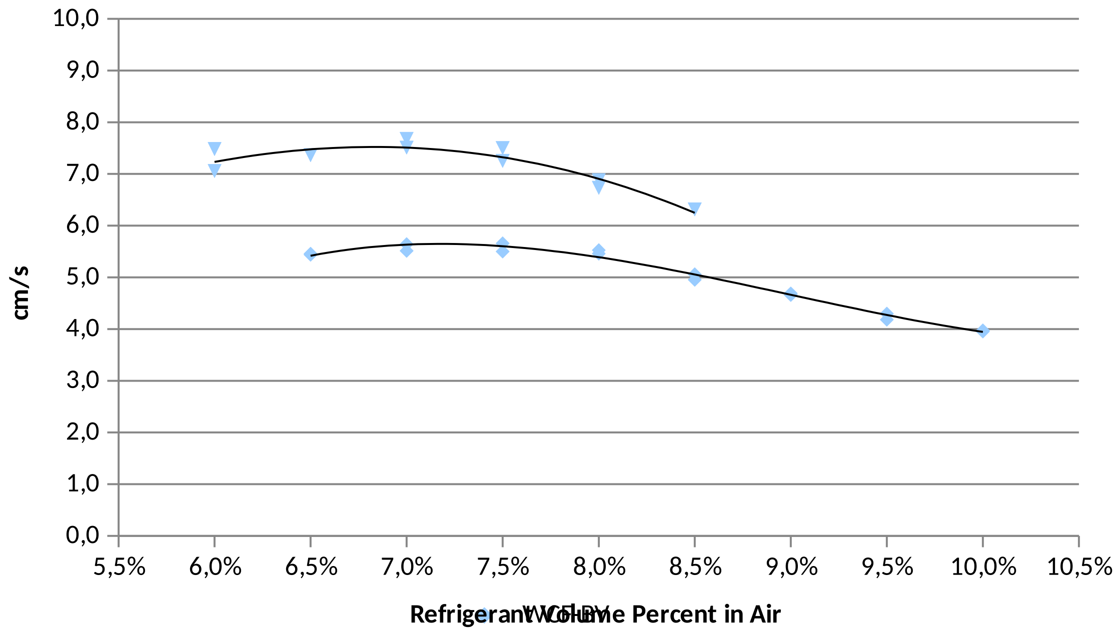

Figure1: HFOG7 Burning Velocity

Maximum values of 5.65 cm/s for the WCF-BV and 7.46 cm/s for the WCFF-BV were determined.

Lower flammability limit (LFL) characterization for refrigerants was performed using ASTM E681 [3]. A spherical flask was filled with increasing amounts of refrigerant in air and exposed to an energized electrode. Both temperature and humidity were maintained in the flask per the ASTM standard. Flame propagation was determined per the standard to be flame angles of 90 degrees or greater. The last refrigerant concentration prior to flame propagation was determined to be the LFL. Similar to the burning velocity experiments, WCF and WCFF compositions were defined specific to LFL. These compositions were 6.0% R-32, 79.0% R-1234yf, and 15.0% R-152a for WCF-LFL and 0.0% R-32, 81.0% R-1234yf, and 19.0% R-152a for WCFF-LFL. Both compositions were tested at 23°C and 60°C. The lowest LFL resulted from the WCFF-LFL at 60°C and yielded a value of 5.0% v/v in air. For comparison, R-1234yf LFL is 6.2% v/v in air

4.2 Fractionation Analysis

To determine the WCFF values for both LFL and burning velocity, Refleak Version 6.0 [4] was employed to model specific leak scenarios per ASHRAE Standard 34. Laboratory experiments were conducted to validate the modeling results. As an example, with the starting composition of the WCF-LFL (6.0/79.0/15.0 R-32/R-1234yf/R-152a by weight %), a cylinder was modeled with an initial liquid fill at 54.4°C to 90% of the total volume. A leak of the cylinder was then simulated at -26.1°C. These results can be seen below.

Table9: Leak Simulation, -26.1°C and 15% fill

	Liquid Composition			Vapor Composition		
% Loss	R-32	R-1234yf	R-152a	R-32	R-1234yf	R-152a
0	6.0	79.0	15.0	18.5	69.9	11.6
2	5.7	79.2	15.1	17.9	70.4	11.7
10	4.7	79.9	15.4	15.4	72.3	12.3
20	3.6	80.7	15.7	12.3	74.7	13.1
30	2.6	81.4	16.0	9.2	77.0	13.8
40	1.7	82.0	16.3	6.4	79.1	14.5
50	1.1	82.3	16.6	4.0	80.8	15.2
60	0.6	82.6	16.9	2.2	82.1	15.7
70	0.2	82.6	17.2	1.0	82.8	16.2
80	0.1	82.4	17.6	0.3	83.0	16.7
90	0.0	81.8	18.2	0.0	82.7	17.3
95	0.0	81.3	18.7	0.0	82.3	17.7

The simulated scenario was replicated in the lab and the results of both methods were plot together as a validation below. The model was well aligned with the experimental results ensuring the simulated WCFF compositions were accurate.

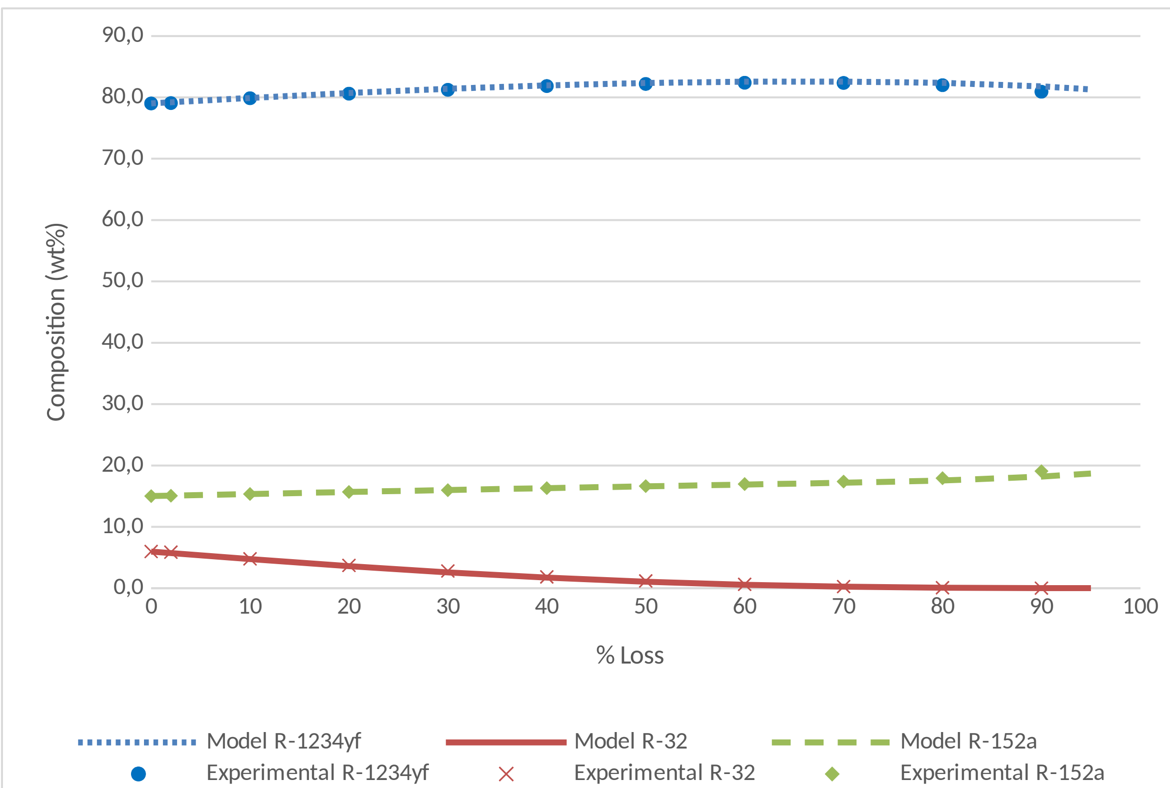

Figure2: Comparison of Experimental and Model Liquid Data, 90% Fill, -26.1°C

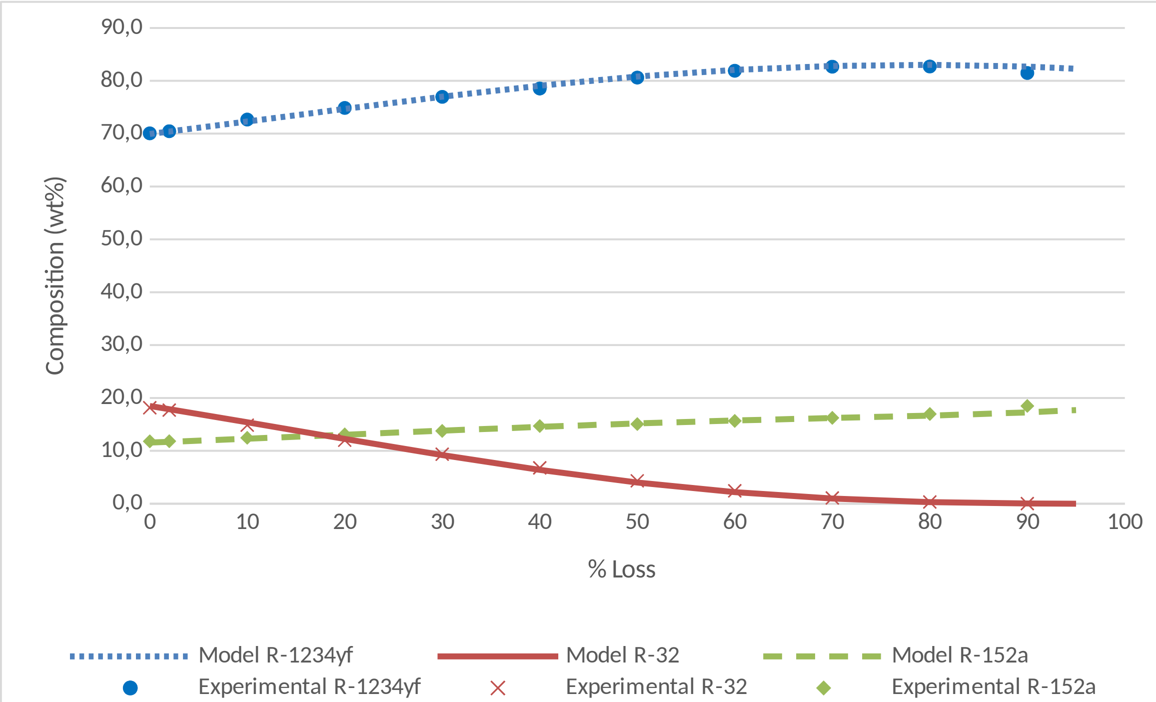

Figure3: Comparison of Experimental and Model Vapor Data, 90% Fill, -26.1℃

5 Conclusion

Addressing the thermal management deficiencies in BEVs is a key issue for the automotive OEMs where they have identified that both improvements in heating capacity and system efficiency are needed. As the adoption of heat pumps for BEVs becomes mainstream, improvements provided by novel refrigerant HFOG7 will aid in bridging this gap. HFOG7 has shown significant improvements in both volumetric heating and cooling capacity, 25.1% and 22.6% respectively, as well as COP over R-1234yf, the incumbient refrigerant. It has a low GWP of 72, exhibits low glide and meets the classification of A2L by ASHRAE. As the HFOG7 blend relies on R-1234yf as the main constituent, it is able to capture the benefit of being low GWP fluid and having suitable performance in air conditioning mode. The additions of R-32 and R-152a provide impovements in both volumetric capacity and system efficiency respectively. Overall, the blend is able to enhance the performance of a heat pump system in both hot and cold ambient climtes, establish good material compatibility for plastics and elastomers and demonstrate stability through extreme conditions and temperatures. These characteristics will enable HFOG7 to be used successfully in next generation heat pump systems for electric vehicles.

Acknowledgments

We would like to acknowledge our laboratory professionals at Chemours Discovery Hub – Partick, John, Hugh and Carol. Without your hardwork and dedication, we would not be able to present the data for our new HFOG7 fluid blend. Thank you!

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