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## A Non-Flammable, Reduced GWP, HFC-134a Replacement in Centrifugal Chillers: DR-11

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### ABSTRACT

Air conditioning in large buildings is often provided by centrifugal chillers using HFC-134a. Efforts to mitigate climate change are motivating the identification of HFC replacements with low GWPs. HFO-1234yf, with a  $GWP_{100}=4$ , has been found promising as an HFC-134a replacement in centrifugal chillers (Kontomaris *et al.*, 2010). However, HFO-1234yf is marginally (ASHRAE 2L) flammable. A new non-flammable developmental refrigerant, DR-11, with a  $GWP_{100}<600$ , was evaluated as an HFC-134a replacement in centrifugal chillers. Given the minimal refrigerant emissions from chillers and its higher predicted energy efficiency, DR-11 could enable solutions with comparable or even lower total global warming impact than HFO-1234yf despite its higher GWP. Moreover, the higher predicted DR-11 refrigeration capacity and the lack of DR-11 flammability may allow more cost-effective solutions than HFO-1234yf that can be adopted without any delays for safety code revisions. Flexible climate change regulations would allow acceptance of refrigerants with optimum performance, flammability and GWP trade-offs.

### 1. INTRODUCTION

Comfort air conditioning consumes a large fraction of the total electricity used in commercial and institutional buildings which in turn contribute substantially to total energy consumption and climate change. Air conditioning in large buildings and complexes such as hospitals, office buildings, hotels, shopping malls and university campuses is commonly provided by large tonnage centrifugal water chillers. In general, centrifugal chillers dominate in applications requiring over 2,275 kW (647 RT) of cooling capacity (UNEP Report, 2006). Centrifugal chillers are also used to provide process cooling in industrial applications. They operate according to the classical vapor-compression refrigeration cycle. They use centrifugal compressors to elevate the pressure of the refrigerant vapor sufficiently to allow rejection of its heat of condensation at near-ambient temperatures.

CFC-11, CFC-12, R-500 and HCFC-22 were the refrigerants predominantly used in centrifugal chillers before the adoption of the Montreal Protocol in the late 1980s. The industry migrated mostly to HCFC-123 and HFC-134a, respectively, in the early 1990s. Centrifugal chillers using HCFC-22 rarely were produced after the late 1990s. The conversion of suitable candidates among pre-existing chillers employing CFC refrigerants to the new refrigerants has largely ended. The replacement of aging CFC-based chillers by new more energy efficient HCFC-123 and HFC-134a chillers continues. According to a relatively recent estimate (UNEP Report, 2006) there are over 130,000 centrifugal chillers in operation around the world with a total refrigerant bank of about 60,000 tons. The estimated

size of the world centrifugal chiller market in 2004 was approximately 8,500 units annually, including 3,500 in the U.S., 1,500 in China, 550 in Europe, 400 in South Korea and Japan, and 300 in the Taiwan region.

Escalating efforts to limit Greenhouse Gas (GHG) emissions around the globe are resulting in growing pressure on the use of Hydro-Fluoro-Carbons (HFCs) and are motivating a search for HFC replacements with lower global warming potentials (GWPs). For example, the European Union adopted the F-Gas regulation requiring that air conditioning systems for new automobile models use refrigerants with GWPs lower than 150 starting in 2011. The F-Gas regulation is scheduled for review and update in 2011. In preparation for the review, potential regulations on stationary applications of HFCs are under consideration. Climate change regulations in various forms are under consideration in many countries around the world.

Hydro-Fluoro-Olefins (HFOs) have been identified as a class of low-GWP compounds with the potential to replace HFCs in various applications. For example, HFO-1234yf, with a 100 year horizon  $GWP_{100}=4$ , has found widespread acceptance as a replacement for HFC-134a in automobile air conditioning (SAE Press Release, 2009). HFO-1234yf has also been found promising as a replacement for HFC-134a in centrifugal chillers (Kontomaris and Leck, 2009 and Kontomaris *et al*, 2010).

HFO-1234yf is marginally flammable (ASHRAE Standard 34 class 2L). A risk assessment by SAE in 2009 found that the risk of injury as a result of HFO-1234yf ignition from an automobile collision is very low and much lower than other widely accepted everyday risks. However, the risks involved in chiller operation do not fully overlap with those addressed by the SAE assessment. For example, the refrigerant charge in chillers is much larger than that used for automobile air conditioning, thus seemingly increasing the flammability risk. On the other hand, chillers are usually kept in machine rooms with ventilation and refrigerant sensors in place and are operated by trained technicians, all factors that could mitigate the flammability risk and ensure safety without undue additional costs. Chiller-specific studies are required to assess the flammability risk resulting from the use of HFO-1234yf.

The adoption of HFO-1234yf for use in centrifugal chillers or other stationary applications that currently use non-flammable refrigerants would require the development of standards for the safe use of 2L flammable refrigerants and revisions of applicable safety codes. The committee for ASHRAE Standard 15, Underwriters Laboratory and the EN378 group in Europe are already considering standard revisions to accommodate the new 2L flammability classification. However, a lengthy process is anticipated before local building and safety codes in various regions are adapted.

The objective of this paper is to introduce a new non-flammable, low GWP developmental refrigerant, DR-11, and evaluate its potential to replace HFC-134a in existing and new centrifugal chillers. DR-11 is an azeotrope containing HFO-1234yf.

## 2. METHODS

The thermo-physical properties of DR-11, including component interaction parameters, were determined from measurements of a few key properties including the liquid density and vapor pressure over a wide temperature range. The property estimation methodology has been described by Leck (2009). It is based on proprietary group contribution methods and equations of state validated through comparisons with measured refrigerant properties. System model results for developmental refrigerants are also validated by comparing with calorimetric and psychrometric environmental chamber measurements. The accuracy of the predicted properties for developmental refrigerants is continually improved as new measurements become available. Determining the transport properties of DR-11 and their impact on overall chiller performance were outside the scope of this paper.

The thermodynamic performance of DR-11 in a typical large tonnage chiller cycle was computed and compared with other mid-pressure refrigerants, namely, CFC-12, HFC-134a and HFO-1234yf. The evaporator and condenser temperatures were specified as 4.4 °C (40 °F) and 37.8 °C (100 °F), respectively. The liquid sub-cooling at the condenser exit, the vapor superheat at the evaporator exit and the pressure drops in connecting pipes were assumed negligible. The compressor isentropic efficiency was specified as 0.70.

The safety, health and environmental properties of the new refrigerant as well as its thermal and chemical stability and compatibility with lubricants and common materials of chiller construction were assessed through standard testing procedures, as described in the results section.

### 3. RESULTS

#### 3.1 Basic Properties and Vapor-Liquid Equilibrium

Table 1 compares key properties of DR-11 to CFC-12, HFC-134a and HFO-1234yf. A safety rating of A1 according to ASHRAE Standard 34 would be expected for DR-11. The ozone depletion potential (ODP) of DR-11 is zero and its 100 year horizon GWP is less than 600, more than 58% lower than that of the incumbent refrigerant, namely HFC-134a. The critical temperature,  $T_{cr}$ , of DR-11 is only slightly lower than that of HFC-134a and comfortably higher than ambient temperatures.

Table 1: Basic properties of DR-11 compared to CFC-12, HFC-134a and HFO-1234yf

Property	CFC-12	HFC-134a	HFO-1234yf	DR-11
Chemical Formula	$\text{CCl}_2\text{F}_2$	$\text{CH}_2\text{F}-\text{CF}_3$	$\text{CF}_3\text{CF}=\text{CH}_2$	Azeotrope
MW	120.91	102.03	114.04	undisclosed
Toxicity Class (ASHRAE Std 34)	A (Low)	A (Low)	A (Low)	A (Low, expected)
Flammability Class (ASHRAE Std 34)	1 (Non Flammable)	1 (Non Flammable)	2L (Low Flammability)	1 (Non Flammable)
ODP	1.00	0.00	0.00	0.00
GWP <sub>100</sub> (100 yr integration horizon)	10,890	1430	4	less than 600
$T_{cr}$ [°C]	112.0	101.1	94.7	97.5
$P_{cr}$ [MPa]	4.14	4.06	3.38	3.82
$T_b$ [°C]	-29.8	-26.1	-29.5	-29.2
Chiller Glide [°C]	N/A	N/A	N/A	No greater than 0.01

The components of DR-11 form nearly azeotropic mixtures over a wide range of compositions and temperatures. The boiling point,  $T_b$ , of DR-11 under atmospheric pressure is within about 3% of that of HFC-134a. The DR-11 composition is azeotropic at both the evaporator and the condenser temperatures of a typical centrifugal chiller. The temperature glide in either the evaporator or the condenser of a DR-11 chiller is expected not to exceed 0.01 °C.

Figure 1 compares the vapor pressure of DR-11 to the vapor pressures of CFC-12, HFC-134a and HFO-1234yf over a wide temperature range including the range pertinent to water chiller operation. DR-11 generates slightly higher pressures (by 5% and 9% at the assumed condenser and evaporator temperature, respectively) but requires a 3.5% lower compression ratio than HFC-134a. For comparison, HFO-1234yf generates vapor pressures that match that of HFC-134a at the condenser and exceed that of HFC-134a at the evaporator by 6%; it requires a compression ratio 5.8% lower than HFC-134a.

#### 3.2 Thermodynamic Cycle Performance

Figure 2 compares the predicted pressure-enthalpy diagram of DR-11 to other mid-pressure centrifugal chiller refrigerants. It shows that the DR-11 pressure-enthalpy diagram approaches that of HFC-134a more closely than HFO-1234yf (or CFC-12). The performance of DR-11 as well as CFC-12, HFC-134a and HFO-1234yf in a cooling cycle typical of chiller operation was estimated using the pressure-enthalpy relationships in Figure 2. Key state variables and performance metrics relative to the currently and previously used mid-pressure chiller refrigerants, namely HFC-134a and CFC-12, are summarized in Table 2.

The compression work (i.e. isentropic compression enthalpy rise) required to lift a unit mass of DR-11 from evaporator to condenser conditions is estimated to be 11.7% lower than HFC-134a. The tip speed,  $V_{tip}$ , of the impeller of a centrifugal compressor required to impart to the fluid a specified amount of compression work can be estimated as:

$$V_{tip} = \sqrt{\frac{\Delta \hat{h}_{comp}}{\mu}} \quad (1)$$

where,  $\mu$ , is the work coefficient and,  $\Delta \hat{h}_{comp}$ , is the enthalpy of compression per unit mass of the working fluid (ASHRAE Handbook, 2008). The work coefficients for all refrigerants considered in this paper were assumed equal; therefore, relative values of the impeller tip speed do not depend on the assumed value of the work coefficient. Then, if a centrifugal compressor were used, a 6% lower impeller tip speed would suffice for DR-11 relative to HFC-134a. The compressor discharge temperature would be 9.8% lower with DR-11 relative to HFC-134a. The net refrigeration effect across the evaporator per unit mass of DR-11 would be 13.9% lower than HFC-134a. However, the DR-11 vapor density at compressor suction conditions is 17.8% higher than HFC-134a. The higher DR-11 vapor density compensates for its lower net refrigeration effect and results in a 1.5% higher volumetric cooling capacity for DR-11 compared with HFC-134a. The coefficient of performance, COP, is defined as the ratio of the rate of heat withdrawal at the evaporator (i.e. useful cooling delivered) and the power consumed by the compressor. The COP with DR-11 is about 2.5% lower than HFC-134a. Use of DR-11 leads to a higher COP than HFO-1234yf because DR-11 delivers an 11.6% larger refrigeration effect than HFO-1234yf while it requires only 9.2% more work of compression per unit mass. The volumetric cooling capacity of DR-11 is 8.5% higher than HFO-1234yf.

The results in [Table 2](#) suggest that large tonnage centrifugal chillers using DR-11 could be designed with performance comparable to that of currently used HFC-134a chillers. Replacing HFC-134a with DR-11 in existing chillers also seems feasible. The potential of the new refrigerant to replace HFC-134a in centrifugal chillers was further assessed by examining the impact of refrigerant choice on centrifugal compressor operation. Compressor operation was described in terms of the compression enthalpy,  $\Omega$ , and the refrigerant volumetric flow rate at compressor inlet conditions,  $\Theta$ , both made dimensionless using the impeller diameter,  $D$ , and the speed of sound,  $\nu$ , in the vapor entering the compressor:

$$\Omega = \frac{\Delta \hat{h}_{comp}}{\nu^2}; \quad \Theta = \frac{\dot{Q}}{\nu \cdot D^2} \quad (2a \& b).$$

An impeller diameter to be used in equation (2b) was determined by the requirement that the impeller simultaneously provide the tip speed and volumetric flow rate required for a selected refrigerant to lift heat from the specified evaporator temperature to the specified condenser temperature at a rate that meets a specified cooling duty:

$$D = \sqrt{\frac{\pi \cdot \dot{Q}}{\phi \cdot V_{tip}}} ; \quad \Theta = \frac{\phi}{\pi \cdot \sqrt{\mu}} \cdot \frac{\sqrt{\Delta \hat{h}_{comp}}}{\nu} \quad (3a \& b)$$

where,  $\phi$ , is the impeller flow coefficient defined in the ASHRAE Handbook (2008). The flow coefficients for all refrigerants considered in this paper were assumed equal; therefore, relative values of the impeller diameters do not depend on the assumed value of the flow coefficient. [Table 2](#) shows the relative values of the calculated impeller diameters. The impeller required for DR-11 would be 2.4% larger than HFC-134a. For comparison, by the same analysis HFO-1234yf would require an impeller diameter 9% larger than HFC-134a and HFC-134a would require an impeller diameter 7.7% smaller than CFC-12.

[Figure 3](#) shows the relative positioning of the operating points of a centrifugal compressor operating with DR-11, HFO-1234yf, HFC-134a or CFC-12. The  $\Omega$ - $\Theta$  coordinates of the points in [Figure 3](#) were calculated using equations 2a and 3b. Despite the simplistic estimation procedure leading to [Figure 3](#), it can be concluded that replacing HFC-134a with DR-11 would require a smaller adjustment in the compressor operation than with HFO-1234yf. The required adjustment with either DR-11 or HFO-1234yf appears smaller than that required for replacing CFC-12 with HFC-134a.

### 3.3 Miscibility with Lubricants

HFC-134a is commonly used with polyol ester (POE) type lubricating oils. Most of the POE refrigeration lubricants are based totally or partially on esters of pentaerythritol,  $C(CH_2OH)_4$ . The miscibility of DR-11 with three commercially available chiller POE lubricants (two ISO32 and one ISO68) was tested over a wide range of concentrations and temperatures that covers the operating ranges typically encountered in centrifugal chillers. Sealed glass tubes containing DR-11 and lubricant in various proportions were prepared and immersed sequentially first in a cold and then in a warm agitated constant temperature bath controlled at the targeted temperature levels. The miscibility characteristics of each DR-11/lubricant blend were visually observed and recorded, after temperature equilibration, at temperature increments of 5 °C. Blends with a homogeneous, translucent solution appearance were qualified as “miscible” at the observation temperature. Blends separating into distinct phases divided by a meniscus or exhibiting turbidity (i.e. cloudiness or haziness) indicative of the formation of individual particles were designated as “non-miscible”. Mixtures of DR-11 with 5 to 70 wt% of the selected POE lubricants were completely miscible over the temperature range representative of centrifugal chiller operation.

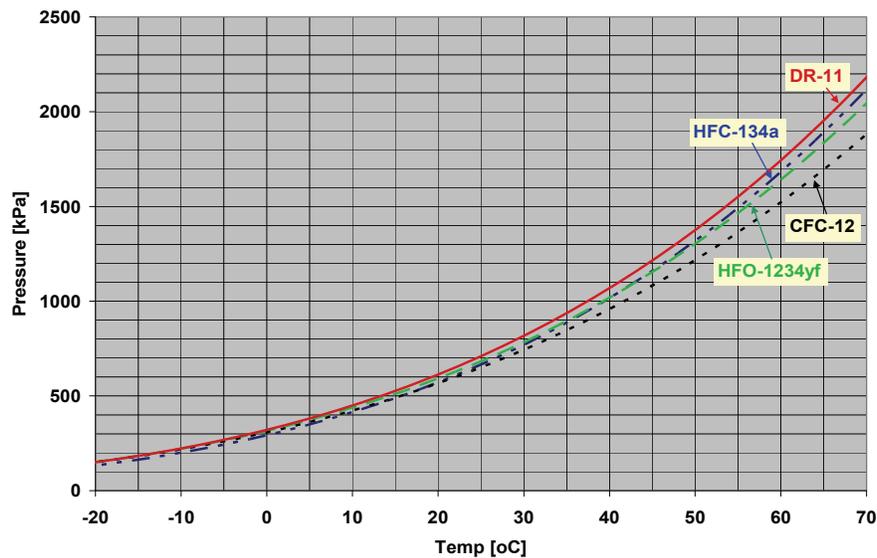


Figure 1: DR-11 vapor pressure curve compared to other mid-pressure chiller refrigerants

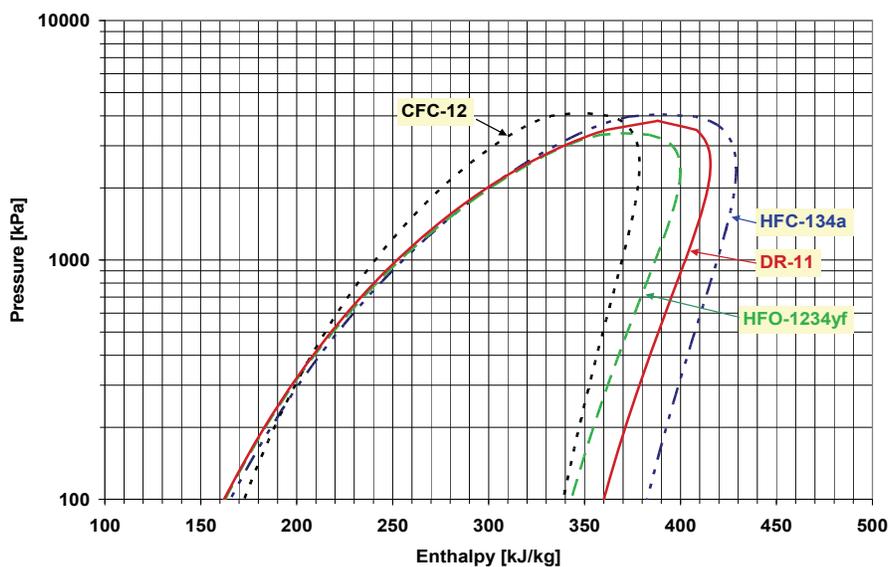


Figure 2: DR-11 pressure-enthalpy diagram compared to other mid-pressure chiller refrigerants

Table 2: Predicted thermodynamic cycle performance of DR-11 and HFO-1234yf relative to HFC-134a; also cycle performance of HFO-1234yf and HFC-134a relative to CFC-12  
 ( $T_{\text{eva}} = 4.4$  [°C];  $T_{\text{cond}} = 37.8$  [°C];  $\Delta T_{\text{subc}} = 0$  [°C];  $\Delta T_{\text{superh}} = 0$  [°C];  $\Delta P = 0$  [Pa])

	DR-11 vs HFC-134a %	HFO-1234yf vs HFC-134a %	HFC-134a vs CFC-12 %	HFO-1234yf vs CFC-12 %
Compression Ratio	-3.5	-5.8	9.5	3.2
Compressor Enthalpy Rise	-11.7	-19.1	29.5	4.8
Compressor Impeller Tip Speed	-6.0	-10.1	13.8	2.4
Compressor Discharge Temperature	-9.8	-15.9	-4.5	-19.7
Net Refrigeration Effect per Unit Mass of Refrigerant	-13.9	-22.8	27.4	-1.6
Vapor Density at Compressor Suction	17.8	21.2	-19.1	-2.0
Cooling Capacity Per Unit Volume of Refrigerant	1.5	-6.5	3.1	-3.6
Coefficient of Performance for Cooling	-2.5	-4.5	-1.7	-6.1
Compressor Impeller Diameter	2.4	9.0	-7.7	0.7

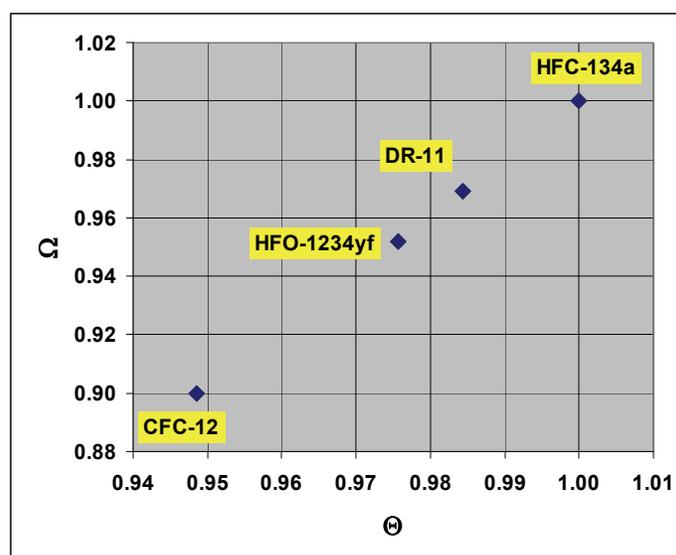


Figure 3: Centrifugal compressor operation with DR-11, HFC-134a, HFO-1234yf and CFC-12.

### 3.4 Thermal Stability and Compatibility with Materials of Chiller Construction

The stability of DR-11 in the presence of materials that it would likely encounter in practical use was scrutinized according to the sealed tube testing methodology of ANSI/ASHRAE Standard 97-2007. Sealed glass tubes containing steel, copper and aluminum coupons immersed in DR-11 were aged for two weeks at 175 °C and compared to similarly prepared and aged sample tubes containing HFC-134a. Visual inspection of the tubes indicated no color change, residues or other deterioration of either refrigerant. Moreover, chemical analysis after thermal aging indicated no detectable fluoride or acid generation. At the test conditions, DR-11 shows stability comparable to that of HFC-134a. Since test conditions were significantly more severe than chiller operating conditions, it can be inferred that DR-11 is sufficiently stable for use in commercial chillers.

The stability of DR-11 in the presence of POE lubricant was also evaluated. Blends containing 50 wt% DR-11 in pre-dried and de-aerated POE lubricant were aged in sealed tubes with immersed steel, copper and aluminum coupons for two weeks at 175 °C and compared to similarly prepared and aged blends containing HFC-134a. No degradation of either the refrigerant-oil blends or the metal coupons was observed. Chemical analysis after exposure indicated no detectable fluoride or acid generation or significant change by Gas Chromatography-Mass Spectroscopy.

The chemical compatibility of DR-11 with plastic and elastomeric materials of construction has not yet been directly tested. However, the compatibility of the components of DR-11 with a wide range of plastics and elastomers has been thoroughly assessed. Sealed glass tubes containing individual DR-11 components and immersed samples of various plastics and elastomers were exposed to temperatures of 100 °C for 2 weeks. The list of tested plastics included polyester resin, nylon resin, epoxy resin, polyester PET, polyester PBT, polycarbonate, polyimide, polyethylene, PTFE, FEP, ETFE, phenolic resin, acetal resin, and PET film. The list of tested elastomers included neoprene WRT, HNBR, NBR, EPDM (Nordel), silicone, butyl rubber, terminal seal, Buna S (SBR), Viton, Hypalon, and neoprene o-ring. The change of the plastic and elastomer sample weights was measured both immediately at the end of the high temperature exposure and after the samples were allowed to recover for 24 hours at room temperature. The specimen weight change could be considered as an indicator of the degree to which additional material properties, such as mechanical strength or permeability, would be expected to change under service conditions. The linear swell and hardness change of the elastomeric specimens was also measured. The test results indicate that the variation of the measured sample properties resulting from exposure to DR-11 components was comparable or less severe than that resulting from exposure to HFC-134a. Given the absence of chemical interactions between the DR-11 components under thermal and chemical stability testing, it can be inferred with relative confidence that DR-11 would be compatible with plastics and elastomers that are known to be compatible with HFC-134a.

### 3.5 Safety, Health and Environmental Properties

Based on the known toxicity characteristics of the DR-11 components, a low toxicity “A” DR-11 rating would be expected according to ASHRAE Standard 34. The atmospheric chemistry and key related environmental properties of DR-11 can be inferred from the well understood atmospheric chemistry of its components. The atmospheric chemistry of DR-11 is expected to lead to the same low GWP breakdown products as HFC-134a. The flammability of DR-11 has been tested at 60 °C according to the ASTM 681-01 procedure outlined in ASHRAE Standard 34 (2007); DR-11 is non-flammable.

## 4. CONCLUSIONS AND DISCUSSION

DR-11 is a developmental refrigerant under consideration as a potential replacement of HFC-134a in both existing and new centrifugal chillers. It is a nonflammable azeotrope containing HFO-1234yf with low toxicity, attractive environmental properties, thermodynamic properties that match closely those of HFC-134a, excellent stability and broad compatibility with chiller lubricants and materials of construction. It has a higher volumetric cooling capacity and COP and approximates HFC-134a chiller performance more closely than HFO-1234yf, another potential low GWP refrigerant for chiller applications.

The GWP of DR-11 ( $GWP_{100} < 600$ ) is less than half of the GWP of HFC-134a ( $GWP_{100} = 1430$ ) but substantially higher than the GWP of HFO-1234yf ( $GWP_{100} = 4$ ). The emissions of refrigerants from chillers can be limited to below 0.5% of the refrigerant charge per year (Calm, 2006). As a result, when fossil fuels dominate the fuel mix used to generate the electricity that supplies a chiller, the primary contribution to global warming from the chiller operation originates from its energy consumption. Given the higher energy efficiency of DR-11 relative to HFO-1234yf, DR-11 may enable new chiller designs and retrofits with comparable or even lower global warming impact than HFO-1234yf, despite its higher GWP, due to its higher predicted energy efficiency.

It is reasonable to anticipate that climate protection legislation may be enacted in various regions around the world in the not-too-distant future to mitigate the impact of stationary air-conditioning (and refrigeration) on global warming. The case study in this paper demonstrates that flexibility in emerging climate change (and safety) regulations will be key in allowing the selection of refrigerants with the optimum trade-offs between cost, flammability, and environmental impact for specific applications. For example, DR-11 may be preferred over HFO-

1234yf for a minimally emissive application, such as chillers, despite its higher GWP because of its performance advantages and its lack of flammability. Adoption of DR-11 in applications currently requiring non-flammable refrigerants and realization of associated environmental benefits would not require any potentially protracted revision of safety codes. However, regulations imposing too-low a GWP cap could preclude DR-11 as an option.

In the absence of regulatory clarity, the formulation and evaluation of candidate refrigerants with a range of attributes (including GWP) is continuing to establish the range of feasible options and inform new system design and climate protection policy. Future work should assess transport effects, test and optimize system performance, and compare cradle-to-grave Life-Cycle Climate Performance.

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