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Overview of novel GWP 1 HFO Refrigerant 1132E and the Mixture of 1132E and R-1234yf

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ABSTRACT

As the world and the US proceeds with HFC phasedown under the Kigali amendment and the US AIM Act respectively, there is growing need novel refrigerant molecules and blends that achieve lower global potential while maintaining or improving on performance. This paper provides an overview of novel GWP 1 HFO refrigerant 1132E and the binary mixture of 1132E and R-1234yf. Specifically, the critical parameters, vapor pressures and saturated densities, flammability classification and properties, stability studies, initial materials and oil compatibility screening. And finally, the paper will present theoretical and laboratory validated refrigerant cycle performance properties of a specific binary blend for replacement of R-134a and R-1234yf in heat pump applications.

1. INTRODUCTION

The 1987 adoption of the Montreal Protocol for the protection of the ozone layer led to the ban of CFC's and eventual phaseout of HCFCs. However the HFC's gases selected to replace the previous generation have been found to have high levels of global warming potential and are considered to be a contributor to global climate change. Taking the next step, the parties to the Montreal Protocol agreed to phase down the use of HFC's, measured in equivalents of CO2 under the Kigali Amendment ratified in 2016. In the United States. The US AIM Act, passed in 2021, seeks a similar 85% reduction in the CO2 equivalents weighted average use of HFC's by 2036.

In order to lower the overall use of HFC's, new innovations in developing molecules with shorter atmospheric lifetimes and therefore lower GWP's are necessary. A class of unsaturated fluorocarbons or HFO's has been identified as meeting those requirements. Unfortunately, the same factors that create lower atmospheric lifetimes that reduce GWP, also have the potential to reduce thermal and chemical stability that was the foundational strength of HFC's. As an example, while having similar thermodynamic properties R-1234yf is less stable and more flammable than the low pressure HFC-134a which it replaced in automotive air conditioning applications.

As we start looking for replacements in other sectors, such as for medium pressure R-404A refrigerant and for high pressure R-410A and R-32 refrigerants we note a sever lack of GWP <1 or HFO refrigerant options as it becomes increasingly difficult to achieve A2L classification for these building blocks as the pressure increases. In this study we will present HFO-1132E ((E)-1,2, Difluoroethylene) as a new high pressure building block for next generation low GWP refrigerant blends and D1V-140 its initial binary blend with R-1234yf. The physical properties initially developed by Higashi et.al are show in Table 1.

Table. 1 physical and safety properties of HFO-1132(E), R-32, R-1234yf and D1V-140

Refrigerant	HFO-1132E	R-32	R-1234yf	D1V-140
Boiling point (101.3 kPa)	-52.5 °C	-51.7 °C	-29.4 °C	-44.6 °C
Critical Temperature	75.6 °C[5]	78.1 °C	94.7 °C	87.1 °C
Critical Pressure	5.16 MPa[6]	5.68 MPa	3.38 MPa	4.04 MPa
Pressure (20°C)	1.46 MPa[6]	1.47 MPa	0.59 MPa	0.94 MPa
ODP	0	0	0	0
GWP (AR5)	0.0056 [4]	677	< 1[1]	<1
ASHRAE Class	B2*	A2L	A2L	A2L*
LFL (Vol %)	4.3	14.4	6.2	5.5
Burning Velocity (cm/s)	32.9	6.7	1.5	2.9

*Scheduled to apply to ASHRAE in 2022

2. Stability Overview

2.1 Sealed Glass Tube Preparation

Accelerated tests were conducted using sealed glass tubes per ASHRAE STANDARD 97. A glass tube having an internal volume of 10 ml was filled with an amount of refrigerant calculated to achieve a pressure of 3.0 MPa during the test, and the glass tube was sealed. When required, a liquid or solid was added to the glass tube before filling with the refrigerant, and the calculated amount of air was filled to coexist with the required amount of oxygen after filling with the refrigerant. The metal coupon test pieces used were a 1.6 x 50 mm round bar. The copper, aluminium, steel round bar (copper was JIS C 3102, steel JIS C 2504 and aluminium JIS H 4040) were prepared. The lubricant used was a commercially available grade. After the test, the refrigerant was collected in a gas sampling bag and used for analysis.

2.2 Analytical Method

The recovered refrigerant was analysed by gas chromatography. In addition, the water-soluble components contained in the recovered refrigerant were absorbed by water and analysed by ion chromatography. This is useful for assessing the amount of hydrogen fluoride produced by any potential decomposition. The total acid value was measured per ASTM D664 to assess the degree of deterioration of the coexisting lubricant.

2.3 Test Condition

The test conditions are shown in Table 2.

Table. 2 Thermal stability test condition of HFO-1132(E) and R-1234yf

ID	Refrigerant	air (oxygen) vol ppm	water ppm	lubricant	metals	temp. ℃	period hour
1	HFO-1132(E)	-	-	-	Cu, Fe,Al	200	120
2	HFO-1132(E)	-	-	-	Cu, Fe,Al	175	336
3	HFO-1132(E)	-	-	-	Cu, Fe,Al	80	1095
4	HFO-1132(E)	500	-	-	-	175	336
5	HFO-1132(E)	-	10^6	-	-	175	336
6	HFO-1132(E)	-	-	-	Cu, Fe,Al	175	336
7	R-1234yf	500	-	-	-	175	336
8	R-1234yf	-	10^6	-	-	175	336
9	R-1234yf	-	-	-	Cu, Fe,Al	175	336
10	HFO-1132(E)	-	-	PVE*	Cu, Fe,Al	175	336
11	HFO-1132(E)	-	-	POE**	Cu, Fe,Al	175	336
12	HFO-1132(E) / R-1234yf	-	-	PVE*	Cu, Fe,Al	175	336
13	HFO-1132(E) / R-1234yf	-	-	POE**	Cu, Fe,Al	175	336
14	R-1234yf	-	-	PVE*	Cu, Fe,Al	175	336
15	R-1234yf	-	-	POE**	Cu, Fe,Al	175	336

*PVE: Polyvinyl ether **POE: Polyol ester

2.4 Results

2.4.1 Thermal Stability

Accelerated testing was performed at 200 ° C for 120 hours or 175 ° C for 336 hours or at 80 ° C for 1095 hours. The results are shown in Table 3.

Table. 3 Results of thermal stability test

ID	Refrigerant	Temp. ℃	Time hour	appearance	purity GC area%	F ion concentration mass ppm
1	HFO-1132(E)	200	120	no change	99.8	2
2		175	336	no change	>99.9	1
3		80	1095	no change	>99.9	1

The appearance of the sealed glass tube after the thermal stability test was observed. Under these conditions, there was no significant change in appearance and no solid matter was produced. No change was observed in the appearance of any of the metal coupons (iron, aluminium, copper). When the sealed tube was opened and the recovered gas was analysed by gas chromatography, no decrease in purity due to the formation of by-products was observed. The recovered gas was brought into contact with pure water to extract water-soluble components such as HF, and the F ion concentration was measured by ion chromatography. As a result, almost no F ion was detected. These results suggest that HFO-1132 (E) is chemically stable even under high temperature conditions and long-term heating conditions.

2.4.2 Effects of coexistence

Comparative tests were conducted to confirm the effects of oxygen, water, and metals, which are potential contaminants that are expected in the actual usage environment. Oxygen introduced at 500 ppm, water was added at 100,000ppm, and metal was evaluated as described above, and the refrigerant after the test was recovered for analysis. The results are shown in Figure 1.

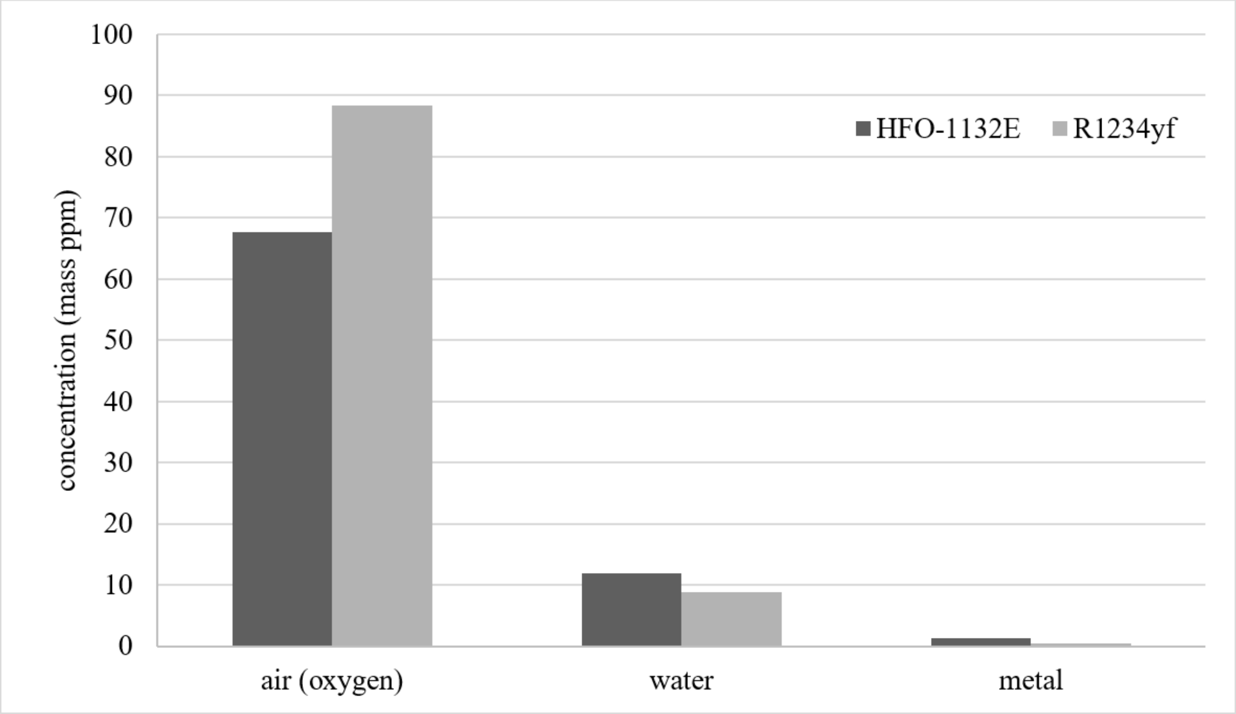


Fig.1 Fluorine ion concentration detected by coexistence of each substance

The amount of detected fluorine ions was converted into the unit weight of the refrigerant and compared with R-1234yf. The fluorine ion concentration was almost the same as that of R-1234yf when evaluating with oxygen, water, and metal coupons. Also, like R-1234yf, oxygen was shown to be a major cause of refrigerant degradation. From this result, it is considered that HFO-1132(E) can be used in the same fashion as R-1234yf.

2.4.3 Exposure tests with Lubricants

Accelerated tests were conducted with lubricant and refrigerant coexisting in a sealed glass tube, and the total acid number was measured to evaluate the degradation of the lubricant collected after the test. The results are shown in Table 4. The test conditions were temperature 175°C, 336 hours, and the refrigerant charge and the amount of coexisting metal were the same as above. There was no change in appearance and no precipitates after the test with either HFO-1132(E) or mixed refrigerant with R-1234yf. In addition, no increase in the total acid number of the lubricants were observed. This result suggests that in the refrigeration cycle system, the refrigerant mixed with HFO-1132 (E) or mixed refrigerant with R-1234yf exists stably, and the performance of the refrigerant will not be altered.

In this test, the water content of the lubricant was 50 ppm and there was no oxygen in the system. Large amounts of water and oxygen are expected to cause negative effects for additives in lubricants. However, as was the case with R-1234yf, implementation of application-specific technical measures would be sufficient to allow for its use.

Table. 4 Results of total acid value of lubricants after thermal stability test.

ID	refrigerant	lubricant	metals	temp. ℃	period hour	appearance	TAN*** mgKOH/g
10	HFO-1132(E)	PVE	Cu, Fe,Al	175	336	no change	<0.01
11	HFO-1132(E)	POE	Cu, Fe,Al	175	336	no change	<0.01
12	HFO-1132(E) / R-1234yf	PVE	Cu, Fe,Al	175	336	no change	<0.01
13	HFO-1132(E) / R-1234yf	POE	Cu, Fe,Al	175	336	no change	<0.01
14	R-1234yf	PVE	Cu, Fe,Al	175	336	no change	<0.01
15	R-1234yf	POE	Cu, Fe,Al	175	336	no change	<0.01

*** Total Acid Number

2.4.4 Solution properties of refrigerant with lubricant

As important compatibility of refrigerant with lubricants other than stability with lubricant, solution properties between refrigerant and lubricant like critical solution temperature, solubility and viscosity are also important. We measured critical solution temperature of the refrigerant with lubricant. Tested refrigerant was a blend composition of HFO-1132(E) and R-1234yf. As polyol ester lubricant, SUNICE SL-68S and SUNICE SL-100T were selected because they are one of the polyol ester lubricants which are commonly used in the world. The results are shown in figure 2-1 and 2-2. We also measured the relationship between refrigerant pressure, solubility to lubricant and lubricant viscosity. The results are plotted in figure 2-1 and 2-2 as PTS diagram and TVS diagram.

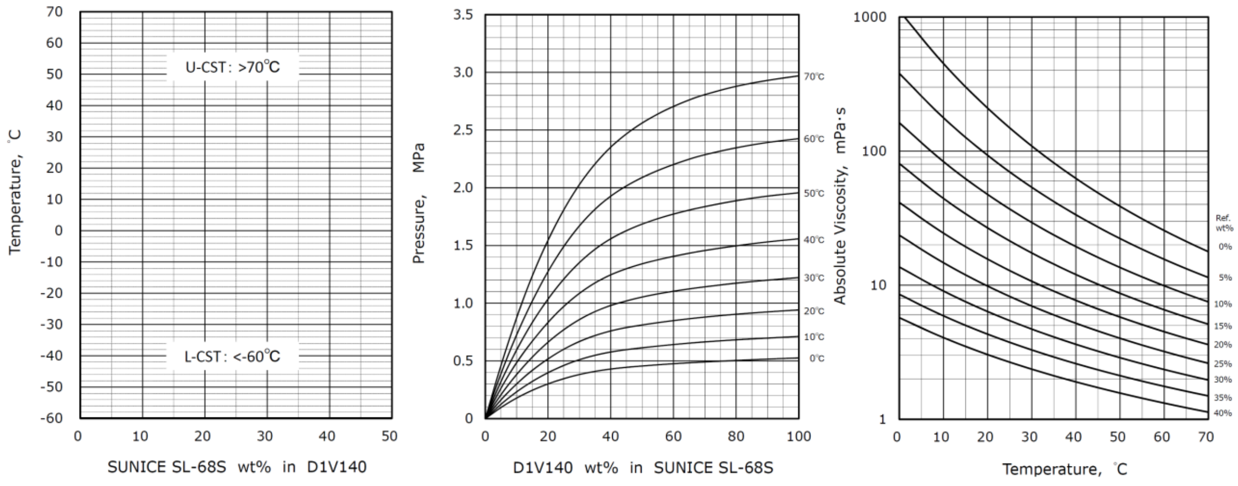


Fig.2-1 Critical solution temperature, PTS diagram and TVS diagram between refrigerant and SUNICE SL-68S

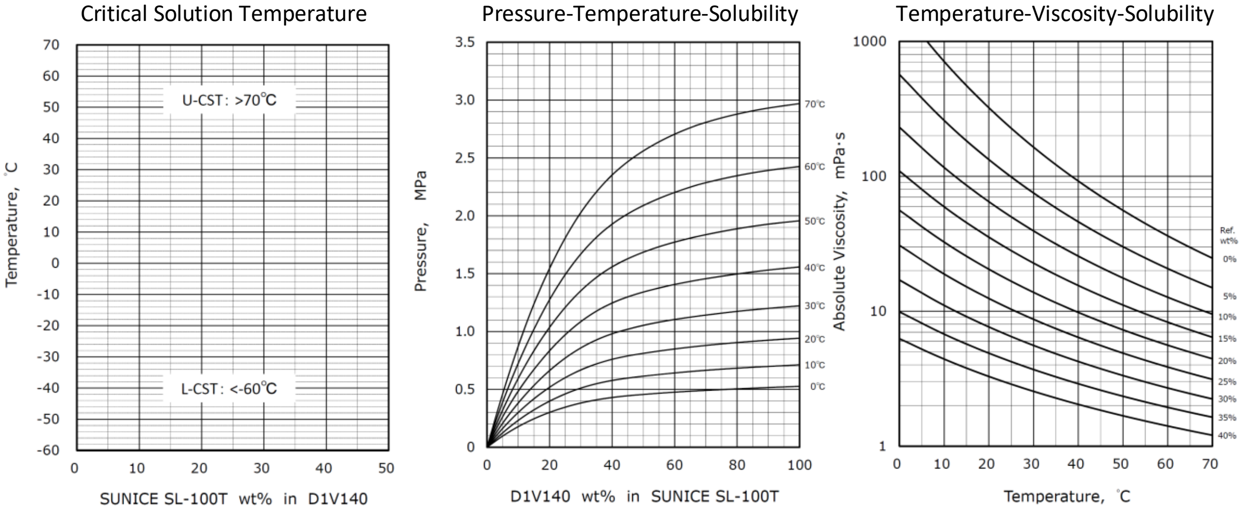
Critical Solution Temperature

Pressure-Temperature-Solubility

Temperature-Viscosity-Solubility

Lubricant: SUNICE SL-68S
Refrigerant: D1V-140

Fig.2-2 Critical solution temperature, PTS diagram and TVS diagram between refrigerant and SUNICE SL-100T



Lubricant: SUNICE SL-100T
Refrigerant: D1V-140

In this test, we found that this blend composition based on HFO-1132(E) has good miscibility with SUNICE SL-68S and SUNICE SL-100T. PTS diagram and TVS diagram do not seem to exhibit extraordinary behaviour.

2.5 Chemical Stability Conclusion

Several evaluations were made on the thermal stability of the new higher pressure HFO-1132(E) both in pure and blended composition. As a result, we observed thermal and oil stability on par or better than R-1234yf. It has been confirmed that HFO-1132(E) has enough stability to withstand use with commonly used substances and at typical refrigeration conditions.

3. Materials Compatibility

3.1 Material Preparation

Materials were selected and prepared per SAE Standard J2670. Materials evaluated are in table 5. Elastomeric materials were prepared into 35mm long dogbone shape and placed into a 200ml cylindrical autoclave in the presence of ND-11 Polyolester Lubricant with D1V-140 Refrigerant and with R-1234yf refrigerant as a control. They were aged at 150°C for 30 days

Table 5. Materials Evaluated

Material	**Grade**
HNBR	KUREHA Corp. – ZB565N
Neoprene (CR)	Osaka Rubber Corp. – 3006
EPDM	KUREHA Corp. – EB270NE
PTFE	NICHIAS Corp. - TOMBO No.9000
Polyester (PBT)	Polyplastics Co. – DURANEX 2002 White

3.2 Analytical Method and Results

The material samples were removed from the autoclave and checked for weight change, thickness change, hardness change 24hrs after removal. The materials were also evaluated for tensile strength change and elongation at break 24hrs after removal. The material and collected oil were also visually inspected. The results are presented in table 6. Weight change, thickness change, and hardness are within CRP150 criteria determined in SAE. Tensile strength change and elongation at break are partially outside the criteria but are equivalent to 1234yf.

Table 6. Materials Testing Summary

	HNBR		Neoprene		EPDM		PTFE		PBT	
	D1V	1234yf	D1V	1234yf	D1V	1234yf	D1V	1234yf	D1V	1234yf
Weight %	-3	-3.1	-4.3	-5.3	-5.5	-5.2	2.1	2.5	2.5	1.7
Thickness %	-6	-2.7	-2.6	-3	-3.7	-2.5	1.9	2.3	1.5	1.3
Hardness %	4.7	6.4	3.1	6.4	12.9	11.6	-9.6	-5.1	-4	-5.5
Tensile Strength (%)	+3	-5	-51	-53	-36	-46	-15	-15	-9	-2
Elongation at break (%)	-27	-29	-55	-53	-46	-45	-13	-13	-70	-82

3.4 Materials Screening Conclusion

HFO1132E and R-1234yf Blend (D1V-140) showed very similar material compatibility properties to R-1234yf when evaluated under the SAE J2670. Future work will expand on materials and material grades as defined by final application and end user in HVAC, Automotive, Refrigeration etc…

4. Modelling and Laboratory performance evaluation of D1V-140

4.1 Modelling

A thermodynamic cycle analysis was performed to assess the ideal cycle performance of D1V-140 versus R-1234yf at various heat pump and air conditioning conditions. Modelling was done utilizing NIST Refprop version 10.0 utilizing the mixture parameters presented by Akasaka and Lemmon. Modelling outcomes are enumerated in Table 8. In general, we see a 33%-46% capacity improvement and a COP match compared to R-1234y. There is a proportionate increase in operating pressures allowing operation down to -30C or below, however still within the expected range for automotive equipment.

4.2 Laboratory Evaluation

Laboratory evaluation was completed utilizing a compressor calorimeter test bench at the Ipetronik Engineering Technical Center utilizing a commercially available automotive compress. The scroll compressor had a displacement of 34 cubic centimetres, ranged in speed from 1500 to 8500 RPM, used standard automotive PAG oil SPA 2, and operated at 400 volts. The calorimeter test chamber was maintained at 70°C. Both heatpump and AC mode conditions were evaluated. Test conditions are show in table 9 and results are detailed in table 10. The compressor results demonstrate significant capacity improvements over R-1234yf across all operating conditions and significant compressor COP improvement specifically in heating operation and high load cooling modes.

5. Conclusion

An introduction of novel GWP 1 HFO molecule 1132E and its binary mixture with R-1234yf, D1V-140 was described. Thermodynamic parameters and ASHRAE classification of HFO-1132E indicate its suitability as a building block for low GWP refrigerant blends. Material compatibility studies, as well as lubricant stability, solubility and pure stability studies indicate the same or better performance compared to R-1234yf. D1V-140 was modeled comparing performance against R-1234yf for heating and cooling performance specifically at some automotive conditions. Modeling indicated a slight improvement in energy efficiency and a gain of 33-46% cooling capacity compared to 1234yf. Modeling results were validated with compressor calorimetry testing which indicated up to a 23% efficiency and up to a 60% capacity improvement at extreme heating conditions.

Table 8. Modelling Results

	Point1		Point2		Point 3		Point 4		Point 8	
Scenario Description	Severe cold Start and operation		Cold Start and operation		Hot weather Start and operation		Sever Hot Weather Start and operation		Cabin dehumidification and reheat	
Mode	Heating		Heating		Cooling		Cooling		Dehumidification	
Evaporating Temperature (°C)	-40		-20		8		3		15	
Condensing Temperature (°C)	55		55		35		45		35	
Superheat	10		10		10		10		10	
Subcooling	5		5		5		5		5	
	R1234yf	D1V-140	R1234yf	D1V-140	R1234yf	D1V-140	R1234yf	D1V-140	R1234yf	D1V-140
COP%	100%	105%	100%	102%	100%	100%	100%	100%	100%	99%
Cooling Capacity (%)	100%	146%	100%	141%	100%	134%	100%	135%	100%	133%
COP	0.99	1.03	1.47	1.51	6.52	6.50	3.73	3.72	9.33	9.26
Mass Flow Rate	325.06	259.42	324.20	265.84	183.19	157.30	225.40	191.70	75.91	65.60
Volume Flow (Suction)	75.12	51.50	39.04	27.69	8.47	6.33	12.20	9.02	2.84	2.14
Compressor Power (kW)	7.09	6.78	5.44	5.32	1.07	1.08	2.01	2.01	0.32	0.32
Condenser/External Coil Power (kW)	14.09	13.78	13.44	13.32	8.07	8.08	9.51	9.51	3.32	3.32
Suction Pressure (psig)	-3.51	0.49	7.29	15.05	44.47	64.73	35.67	53.00	58.71	83.69
Discharge Pressure (psig)	195.31	266.06	195.31	266.06	113.81	157.00	150.82	206.40	113.81	157.00
Discharge Temperature (°C)	80.6	96.2	74.9	87.1	48.2	52.6	59.6	66.3	47.2	50.4

Table 9. Laboratory Test Results

	Condenser (°C)	Evaporator (°C)	Superheat (K)	Subcooling (K)
Cooling 1	40	-1.5	25	5
Cooling 2	69	-1.5	25	5
Heating 1	0	50	10	5
Heating 2	-10	60	10	5

Table 10. Laboratory Test Results

		R-1234yf		D1V-140		% Change	
	RPM	COP	Cap	COP	Cap	COP	Cap
Cooling 1	1500	3.13	1.5	3.15	2.12	101%	141%
Cooling 1	3000	3.45	3.17	3.54	4.44	103%	140%
Cooling 1	5000	3.34	5.48	3.39	7.59	101%	139%
Cooling 2	1500	1.07	0.94	1.09	1.37	102%	146%
Cooling 2	3000	1.39	2.05	1.46	2.96	105%	144%
Cooling 2	5000	1.48	3.60	1.55	5.13	105%	143%
Cooling 2	7000	1.43	5.03	1.52	7.19	106%	143%
Cooling 2	8500	1.37	6.01	1.45	8.59	106%	143%
Heating 1	5000	1.35	2.57	1.48	3.65	110%	142%
Heating 1	7000	1.27	3.54	1.42	5.09	112%	144%
Heating 1	8500	1.19	4.18	1.36	6.08	114%	145%
Heating 2	5000	0.57	1.07	0.67	1.72	118%	161%
Heating 2	7000	0.55	1.55	0.66	2.42	120%	156%
Heating 2	8500	0.52	1.83	0.64	2.88	123%	157%

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