Summer Student Report: Eco gases for future particle gas detectors

Jógvan Kjølbro

kjolbro@gmail.com

Under the supervision of: Giovanna Saviano and Archana Sharma

CERN European Organization for Nuclear Research

Meyrin, Switzerland

Introduction

Many currently used refrigerant gases have a great impact on the environment since they either contribute largely on the greenhouse gas effect, or because they tear the ozone layer, or both. In an attempt to protect the environment, regulations preventing the production and use of certain refrigerant gases has been implemented[1]. Because the gas particle detectors at CERN operate with mixtures containing the regulated refrigerants, actions towards finding new mixtures must be undertaken. The GEM detectors currently operate with an argon/CO_2/CF_4 mixture [2], where CF_4 has a Global Warming Potentian (GWP) of 7390 [3]. Investigations into new gas mixtures has to be performed in order to keep the mixture properties while complying with the regulations. The aim of this project is to discuss some the important properties of gases for particle gas detectors, list and summarize basic properties of eco-friendly refrigerants from the literature, and to make a prediction on selected parameters.

Gas properties

For a gas mixture to be appropriate in a gas detector, it first of all has to apply with the regulations. But its properties must also be appropriate for the specific type of detectors. For example, a gas that is suitable for the RPC detectors may not be fully optimized for the GEM detectors. To better find the appropriate gas for a detector, an understanding of the influence on different parameters is required. This section aims to clarify the most essential parameters for gases.

Global warmth potential and Ozone depletion potential

> *"Measure what can be measured, and make measurable what cannot be measured."*
> *-Galileo Galilei*

In order to estimate the impact of a refrigerant on the environment, the effects has to be quantified. Two important effects are the contribution to the greenhouse effect and the depletion of the ozone layer. The first mentioned effect is measured in Global Warmth Potential (GWP), and is normalized to the effect of CO_2 (GWP = 1), and the effect on the ozone layer is measured in Ozone Depletion Potential (ODP), normalized to the effect of CCl_3F (ODP = 1). The effect of selected refrigerant candidates are listed in table 3.

Stopping power

When a particle passes through a medium, energy is transferred from the particle to the surroundings. The energy lost is typically defined as the stopping power expressed as $\frac{1}{\rho}\left\langle\frac{dE}{dx}\right\rangle$, where ρ denotes the density of the medium, E denotes energy, and x is length. This expression is itself dependent on the momentum p of the particle. In the next section we will show that the particle will experience a minimum energy loss at around $p/Mc \approx 3$, where M is the particle mass, and c is the speed of light. By knowing the average minimum energy loss, we also know the minimum energy the particle loses by passing through a detector. The minimum mean ionization energies for the refrigerants under consideration are summarized in table 2.

Radiation length

The radiation length X_0 is a characteristic length of a medium. It describes both the mean distance required for a high energy electron to lose all but e^{-1} of its energy due to bremsstrahlung, and $^7/_9$ of the mean free path of a e^+e^- pair produced by a high-energy photon[4]. These quantities are also estimated and summarized in table 2.

Ion pair production

When an incoming particle passes through a medium, it will eventually interact with the medium and transfer some of its energy to ionize atoms. In this process, a pair consisting of an ionized atom and a free electrons, is produced. The number of ionization done by an incoming particle per unit length is denoted by N_P, with units of cm^{-1}. Each produced ion pair will have an initial kinetic energy and can themselves produce ion pair, called secondary ion pair production. The sum of the primary and secondary ion pair production per unit length is denoted N_T, and will mainly depending on the material and the incoming particle energy and mass. This parameter is relevant in particle gas detectors as it determines the amount and sizes of avalanches produced by a single incoming particle when the gas is under an amplifying electric field.

Hazards and flammability

Many refrigerants may constitute danger for the user and its environment. The greatest dangers involved are the flammability and toxicity. We have used two standards in categorizing the refrigerants in table 4 and 5. The Ashrae standard **??**

gives each refrigerant a number denoting flammability from 1 (not flammable) to 3 (highly flamable), as well as a letter A (non-toxic) or B (Toxic). The Health Material Hazardous Material Information System (HMIS), rates Healt/ Flamability/ and Physical hazards from 0 (low) to 4 (high).

Compatibility with materials

Some refrigerants are incompatible with certain materials, and can either react violently, or have long term effect. Some refrigerants may even produce toxic decomposition and/or polymerization. Known incompatibilities and toxic byproducts are summarized in Table 4 and 5.

Estimation of Gas Parameters

Stopping power

Quantities such as the minimum ionization energy can be found if the stopping power is known. An approximate expression for moderately relativistic particles in the momentum region $0.1 \leq \beta\gamma = p/Mc \leq 1000$ can be found using the Bethe-Bloch equation, given by [5]

$$\frac{1}{\rho}\left\langle -\frac{dE}{dx}\right\rangle = Kz^2\frac{Z}{A}\frac{1}{\beta^2}\left[\frac{1}{2}\ln\frac{2m_ec^2\beta^2\gamma^2T_{max}}{I^2} - \beta^2 - \frac{\delta(\beta\gamma)}{2}\right] \tag{1}$$

where $\left\langle -\frac{dE}{dx}\right\rangle$ is the mean energy loss per length, ρ is the density of the medium, I is the mean excitation energy, and $\delta(\beta\gamma)$ is the density effect correction function to ionization energy loss. K is a constant given by $4\pi N_A r_e^2 m_e c^2$, and T_{max} is the maximum energy transfer in a single collision, given by

$$T_{max} = \frac{2m_ec^2\beta^2\gamma^2}{1 + 2\gamma m_e/M + (m_e/M)^2}, \tag{2}$$

where M is the mass of the incoming particle.
The mean excitation energy I for a composite medium can be approximated from the composite atoms by the relation[6].

$$I = \exp\left\{\left[\sum_j w_j(Z_j/A_j)\ln I_j\right] / \langle Z/A\rangle\right\} \tag{3}$$

where w_j, Z_j, A_j and I_j is the fraction by weight, atomic number, atomic weight and mean ionization energy, respectively, of the j'th constituent. The shape of the $\delta(\gamma\delta)$ function for non-conducting materials can be approximated by

$$\delta(\gamma\delta) = \begin{cases} 2(\ln 10)X - \bar{C} & \text{if } X \geq X_1; \\ 2(\ln 10)X - \bar{C} & \text{if } X_0 \leq X < X_1; \\ 0 & \text{if } X < X_0; \end{cases} \tag{4}$$

where $X = \log_{10}(\gamma\delta)$. For finding an approximate expression for the parameters $\bar{C}$, X_0 and X_1 based on experimental fits, we refer to [7]. For gasses with momenta below $\beta\gamma$, the density effect correlation function can safely be neglected. A plot of the calculated energy loss for different refrigerants is show in figure 1.

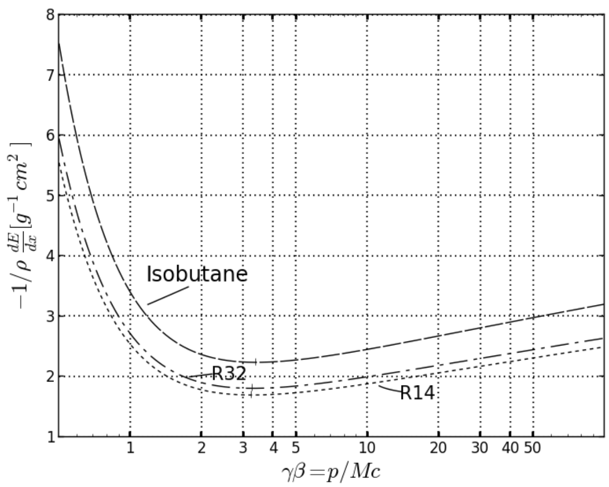

Figure 1: Energy loss function for various refrigerants.

Radiation length

The radiation length of an atom can be found by [4]

$$X_0 = 716.405(\text{cm}^{-2}\text{mol})A/\left[Z^2(L_{rad} - f(z)) + ZL'_{rad}\right] \tag{5}$$

$$f(z) = z^2\sum_{n=1}^{\infty}\frac{1}{n(n^2+z^2)} \approx 1.202z - 1.0369z^2 + \frac{1.008z^3}{1+z} \tag{6}$$

where L_1 and L_2 is given by table , $f(z)$ is the one-photon exchange approximation, and $z = \alpha Z$, α being the fine-structure constant and Z is the atomic number. This formula, however, only holds for free atoms. When one wants to find the stopping power for a molecule, one has to take into account the influence from molecular bindings, crystal structures and polarization of the medium. By neglecting these effects, however, one can find an approximate expression by weighting the radiation length of the single atoms

$$\frac{1}{X_0} = \frac{1}{A_{molecule}}\sum_j\frac{A_j}{X_{0j}}, \tag{7}$$

where j reffers to the j'th atom's constituent.

Z	L_1	L_2
1	5.31	6.144
2	4.79	5.621
3	4.74	5.805
4	4.71	5.924
5≥	$\ln(184.15Z^{-1/3})$	$\ln(1994Z^{-2/3})$

Table 1: L_1 and L_2 expressions for various atom numbers.

Name	I	$-\left\langle \frac{dE}{dx} \right\rangle_{min}$	X_0	N_P
	[eV]	$\left[\text{MeV}\frac{\text{g}}{\text{cm}^2}\right]$	$\left[\frac{\text{g}}{\text{cm}^2}\right]$	$\left[\text{cm}^{-1}\right]$
R32	89.3602	1.80973	35.4581	49.2
R7146	127.401	1.67833	28.6027	92.0
R600a	47.848	2.24057	45.2260	81.0
R1234yf	91.9674	1.7734	35.8204	89.5
R152a	78.1889	1.88706	37.0969	67.1
R1234ze	91.9674	1.7734	35.8204	89.5
R115	116.695	1.69178	29.2197	98.4
R1233zd	106.689	1.73915	29.7636	105
R290	47.0151	2.26184	45.3725	65.2
R13|1	271.737	1.42486	11.5399	272
R134a	95.0294	1.76439	35.1542	81.6
R14	107.127	1.69909	33.9905	63.6
R123	125.275	1.69722	25.5416	98.4
R143a	87.8152	1.8126	35.8928	74.8
R744	88.7429	1.81124	36.1954	37.2
HFE7000	95.0748	1.76365	35.2264	131
HFE7100	96.3202	1.75436	35.1492	146
R23	99.9508	1.7402	34.5214	56.9
R116	105.075	1.70566	34.2947	93.3
RC318	101.578	1.71721	34.8435	123
R218	104.13	1.70873	34.439	117

Table 2: Minimum ionization,radiation length and number of primary ion pair creation for the considered refrigerants, as well as the approximated mean ionization energy used.

Estimation of ionization pair production

In order to model the number of primary ionization caused by a single particle, the cross section for all the particle-atom interaction should be calculated. The number of primary electrons per unit length would then be the integral over energy across all the energy transfer cross sections. This is tedious work since all electron orbital transfers has to be considered. An easier, but more inaccurate correlation between primary ionization and atom number has been found based on experimental data by[8]

$$N_P = 3.996\frac{Z_m}{\bar{Z}^{0.4}} - 0.025\left(\frac{Z_m}{\bar{Z}^{0.4}}\right)\text{cm}^{-1}, \tag{8}$$

which holds for normal pressure and temperature (NPT) (1 atm, 20°C). For different pressure and temperature, the number scales with the density. This value should only be taken as a rough estimation though. This formula has proven to work best for hydrocarbons and worst for molecules consisting mainly of fluorine, differing as much as 30% from the experimental value for CF_4.

The total number of ionization has proven to be more difficult to estimate. Whereas no general formula has been derived, the most straightforward method will be to use the cross sections used to calculate the primary ionization electrons, and use Monte Carlo simulations to track the production of secondary electrons from primary electrons. The total number of pair ionization turns out to be dependent on the incoming particle energy and mass, and a general expression can therefore be difficult to find. For an incoming particle, $W = \frac{\Delta E}{N}$ defines the average energy cost to produce an ion pair. Luckily, this turns out to be a function slowly varying with particle energy[9], and can therefore be taken to be a constant in an energy interval. The total ionization per unit length can then be found by

$$N_T = \rho\frac{dE}{dx}\frac{1}{W} \tag{9}$$

If the W values for specific gases are know, the average W value for a gas mixture can be found by[8]

$$\bar{W} = \sum_m \left[f(n_m)Z(n_m)W(n_m)\right] \Big/ \sum_m \left[f(n_m)Z(n_m)\right], \tag{10}$$

where n_m denotes the index of the molecule, and $f(n_m)$ denotes the relative number of molecules of the given sort in the mixture.

The value of W seems to be very difficult to predict, and there seems to be no direct way to give a proper estimate based on experimental data alone. I therefore propose that a Monte Carlo simulation can be made using the photoabsorption ionization and relaxation (PAIR) model offered by [8]. This will require some work though.

Conclusion

The scope of the project was to summarize various eco friendly refrigerants in one paper. Some properties for these refrigerants have been summarized, either from the literature or calculated from known theory. The hope is that this information can be used in finding new gas mixtures for particle gas detectors that are more environmental friendly while still having the desired properties.

References

[1] United States environmental protection agency. Global anthropogenic non-co2 greenhouse gas emissions.

[2] Archana Sharma. Muon tracking and triggering with gaseous detectors and some applications. *NUCLEAR INSTRUMENTS and METHODS IN PHYSICS RESEARCH SECTION A-ACCELERATORS SPECTROMETERS DETECTORS AND ASSOCIATED EQUIPMENT*, 666:98–129, 2012. ISSN 01689002, 18729576. doi: 10.1016/j.nima.2011.12.001.

[3] "international panel on clima changes". `http://www.ipcc.ch/publications_and_data/ar4/wg1/en/ch2s2-10-2.html`, .

[4] YS Tsai. Pair production and bremsstrahlung of charged leptons. *REVIEWS OF MODERN PHYSICS*, 46(4):815–851, 1974. ISSN 00346861, 15390756.

[5] J. Beringer. 31. passage of particles through matter. Technical report, Particle Data Group, December 2013.

[6] SM Seltzer and MJ Berger. Evaluation of the collision stopping power of elements and compounds for

electrons and positrons. *INTERNATIONAL JOURNAL OF APPLIED RADIATION AND ISOTOPES*, 33 (11):1189–1218, 1982. ISSN 0020708x, 0020738x, 0020708X.

[7] R. M. Sternheimer and R. F. Peierls. General expression for the density effect for the ionization loss of charged particles. *Physical Review B (Solid State)*, 3: 3681–3692, January 1971.

[8] I.B. Smirnov. Modeling of ionization produced by fast charged particles in gases. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment.*, 554(1–3):474 – 493, 2005.

[9] Average energy required to produce an ion pair. Technical report, ICRU Report 31, 1979.

[10] Common Chemistry. http://www.commonchemistry.org/.

[11] "a-gas". http://www.agas.com/upload/product/071113042031_11882.pdf/, .

[12] "united states enviromental protection agency". http://www.epa.gov/ozone/snap/subsgwps.html/, .

[13] H. Kasuya, Y. Kawamura, H. Mizoguchi, Y. Nakamura, S. Yanabu, and N. Nagasaki. Interruption capability and decomposed gas density of cf3i as a substitute for sf6 gas. *IEEE TRANSACTIONS ON DIELECTRICS AND ELECTRICAL INSULATION*, 17(4):1196–1203, 2010. ISSN 10709878, 15584135. doi: 10.1109/TDEI.2010.5539690.

[14] "summary of substitute refrigerants listed in snap notice 25.pdf".

[15] V. W. Bhatkar, V. M. Kriplani, and G. K. Awari. Alternative refrigerants in vapour compression refrigeration cycle for sustainable environment: a review of recent research. *INTERNATIONAL JOURNAL OF ENVIRONMENTAL SCIENCE AND TECHNOLOGY*, 10 (4):871–880, 2013. ISSN 17351472, 17352630. doi: 10.1007/s13762-013-0202-7.

[16] Jitendra Kumar Verma, Ankit Satsangi, and Vishal Chaturani. A review of alternative to r134a (ch3ch2f) refrigerant. 2014.

[17] Air Liquide. Material safety data sheet.

[18] Praxair. Material safety data sheet.

[19] Matheson Tri Gas. Material safety data sheet.

[20] Apollo Scientific Limited. Safety data sheet.

[21] NationalRefrigerants. Material safety data sheet.

[22] Arkema. Technical profile.

[23] Inc. Honeywell. Safety data sheet, .

[24] Inc. Honeywell. Technical information, .

[25] BOC. Material safety data sheet.

[26] HARP International. Material safety data sheet.

[27] Iodeal Brands. Safety data sheet.

[28] Airgas. Material safety data sheet.

[29] The Linde Group. Safety data sheet.

[30] inc. Specialty Gasses Of America. Material safety data sheet.

[31] Inc. Spectra Gases. Material safety data sheet.

[32] LPGenius. Material safety data sheet.

[33] Tesoro Corporation. Material safety data sheet.

[34] Energas. Safety data sheet.

[35] Ferrellgas. Material safety data sheet.

[36] LyondellBasell. Material safety data sheet.

Molecular name	Chemical formula	CAS[10]	Refrigerant identifier	GWP	ODP
Chloropentafluoroethane	C_2ClF_5	76-15-3	R115	7370	0.44
Hexafluoroethane	C_2F_6	76-16-4	R116	-	-
2,2-Dicloro-1,1,1-trifluoroethane	$C_2HCl_2F_3$	306-83-2	R123	120[11]	0[11]
1-Chloro-3,3,3-Trifluoropropene	$C_3H_2ClF_4$	2730-43-0	R1233zd	4.7-7[12]	0[12]
2,3,3,3-Tetrafluoropropene	$C_3H_2F_4$	754-12-1	R1234yf	4[12]	0[12]
1,3,3,3 Tetrafluoropropene	$C_3H_2F_4$	29118-24-9	R1234ze	6[12]	0[12]
Trifluoroiodomethane	CF_3I	2314-97-8	R13|1	23900[13]	0[13]
1,1,1,2-Tetrafluoroethane	CH_2FCF_3	811-97-2	R134a	1430[14]	0[14]
Tetrafluoromethane	CF_4	75-73-0	R14	7390[3]	0
1,1,1-trifluoroethane	CH_3CF_3	420-46-2	R143a	4300[15]	-
1,1-Difluoroethane-1,1-Difluoroethane	$C_2H_4F_2$	75-37-6	R152a	124[14]	0[14]
Octafluoropropane	C_3F_8	76-19-7	R218	-	-
Trifluoromethane	CHF_3	75-46-7	-	12000[15]	-
Propane	C_3H_8	74-98-6	R290	3[14]	0[14]
Difluoromethane	CH_2F_2	75-10-5	R32	650[16]	0[16]
Isobutane	C_4H_{10}	75-28-5	R600a	3[15]	0[15]
Sulfur Hexafluoride	SF_6	2551-62-4	R7146	23000[15]	0.04[15]
Carbon Dioxide	CO_2	124-38-9	R744	1	0[14]
Octafluorocyclobutane	C_4F_8	115-25-3	RC318	-	-
1,1,1,2,2,3,3-Heptafluoro-3-Methoxypropane	$C_4H_3F_7O$	375-03-1	HFE7000	575[14]	0[14]
Methoxynonafluorobutane	$C_5H_3F_9O$	163702-07-6	HFE7100	297[14]	0[14]

Table 3: Summary of various refrigerant candidates.

Refrigerant	Molecular weight	Density	Boiling point	HMIS	Ashare Safety Group
Material incompatibility					
Hazardous decomposition products and polymerization					
R115	154.4	6.623[17]	-39.1[18]	1/0/2[18]	A1
Incompatible with polystyrene, natural rubber, alloys containing more than 2% Mg, oxidizing materials, and acids[18, 19, 20].					
Thermal decomposition can yield toxic fumes of fluorides such as Hydrogen Fluoride, Hydrogen Chloride, Carbon Monoxide, Carbon Dioxide and Chlorine [17, 18, 19, 21].					
R116	138.0	-	-39.1[18]	-	A1
-					
-					
R1233zd	130.5	6.10[22]	-19[23]	2/0/0[23]	-
Incompatible with polyacrylate, Viton®, natural rubber, silicon rubber and other elastomers[22, 24].					
Is considered non-toxic at less than 800 ppm[24]. Hazardous polymerization can occur. If involved in a fire, production under thermal decompose into pyrolysis products containing Hydrogen Fluoride, Carbon Monoxide, Carbonyl halides, and Hydrogen Chloride can occur [23].					
R1234yf	114.0	4.82[25]	-29[25]	0/2/2[23]	-
Incompatible with alkali metals, Zn, Mg and other light metals [26].					
If involved in a fire, production under thermal decompose into pyrolysis products containing Fluorine, Carbon Monoxide, Carbonyl halides, and Hydrogen halides can occur. No toxic decomposition should happen under normal conditions[25, 26].					
R1234ze	114.0	4.82[23]	-29[23]	1/0/0[23]	-
Incompatible with strongly oxidizing materials and finely divided Mg ans Al [23].					
If involved in a fire, production under thermal decompose into pyrolysis products containing Fluorine, Carbon Monoxide, Carbonyl halides, and Hydrogen halides can occur. Polymerization may also occur [23].					
R13|1	195.9	-	-22.5[27]	-	-
Incompatible with active metals, fires of hydrides, and materials containing oxygen [**?**].					
Can decompose to Iodine, Hydrogen Fluoride, and Hydrogen Iodide[**?**].					
R134a	102.0	4.320[18]	-26.5[18]	1/1/0[28]	A1
Chemically reactive with K, Ca, powdered Al, mg, and Zn[21, 29, 30]. Under high temperature/ high pressure, may react with Al surfaces[21].					
Under special circumstances (e.g. high temperature) Carbon monoxide, Carbonyl fluoride, Hydrogen fluoride [18, 21, 25] can be produced. Under normal storage and use, no hazardous decompostion should be produced [25, 28, 29].					
R14	88.0	3.65[17]	-128[17]	0/0/0[17]	A1
Not compatible with aluminium, alloys containing more than 2% magnesium, alkali metals in powdered form and carbon dioxide above 1000 °C [17, 18, 28, 31].					
If involved in a fire, production under thermal decompose into pyrolysis products containing hydrogen fluorid and carbonyl fluoride[17, 18, 28].					
R143a	84.0	-	-47.4[28]	1/4/0[28]	A2
Incompatible with oxidizing materials [28]					
Under normal storage and use, no hazardous decompostion/polymerization should be produced [25, 28, 29].					

Table 4: Table containing information on the refrigerants.

Refrigerant	**Molecular weight**	**Density**	**Boiling point**	**HMIS**	**Ashare Safety Group**
Material incompatibility					
Hazardous decomposition products and polymerization					
R152a	66.1	2.738[28]	-25[19]	1/4/2[28]	A2
Extremely reactive with oxiding materials [28], such as alkaline, alkaline earth metals, and other reactive chemicals, (i.e. Na, K, Ca, Mg, powdered Al, Zn), brass, and steel [17, 25]. Incompatible with amines, bases, and halogens [19].					
Under normal condition, hazardous decomposition and/or polymerization products should not be produced [28]. If exposed to fire, hazardous products may be produced [17]					
R218	188.0	-	-	-	A1
-					
-					
R23	70.0	-	-	-	A1
-					
-					
R290	44.1	1.86[28]	-42[32]	1/4/0[33]	A3
Incompatible with acids, oxygen, oxidizing materials, copper, some plastics, Clorine Dioxide[25, 28, 32, 33, 34, 35].					
Under normal condition, hazardous decomposition and/or polymerization products should not be produced [25, 28]. May produce carbon monoxide and other toxic gasses under thermal decomposition [32, 33, 35].					
R32	52.0	11.4[31]	-51.7[31]	1/4/1[28]	A2
ncompatible with acids and oxidizing materials as Na, K, Ca, Zn, Mg, powdered Al, and other active metals[28, 31]. Incompatible with air and moisture [25].					
No hazardous decomposition/polymerization should be produced under normal conditions [28, 31].					
R600a	58.1	8.93[28]	-11.7[28]	1/4/0[28]	A3
Incompatible with oxiding materials, halogenated hydrocarbons, halogens, and metal catalysts[28].					
No hazardous decomposition/polymerization should be produced under normal conditions [26, 28, 36]. May produce carbon monoxide and other toxic gasses under thermal decomposition [36].					
R7146	146.1	6.17[17]	-63.7[17]	1/0/0[28]	-
Stable with most chemical, except metals other than aluminium, stainless steel, copper brass, silver, at elevated temperatures (>204°C). Also reacts violently with disilane [17, 28].					
Decomposes into Sulfur oxides and hydrogen fluorine [17, 28].					
Refrigerant	Molecular weight	Density	Boiling point	HMIS	Ashare Safety Group
Material incompatibility					
Hazardous decomposition products and polymerization					

Table 5: Table containing information on the refrigerants.