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Natural and synthetic refrigerants, global warming: A review

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ABSTRACT

Halogenated hydrocarbons with high ozone depletion potential (ODP) were banned under Montreal Protocol (1987) due to their detrimental effects on ozone layer that shields the planet against ultraviolet radiations. The greenhouse gases (GHG) used in modern refrigeration, air conditioning, and heat pumping systems, are under Kyoto Protocol (1997)'s time-barred permission period. In order to reduce the depletion of ozone and reverse the climate change effects, the European Union legislation (2014) and Paris Accord (2016) are strongly emphasizing the phasing out of the use of harmful synthetic refrigerants. Choice of natural refrigerants makes no net addition of the greenhouse gases (GHG) in the environment. To retrofit and modify existing cooling and heating systems using natural refrigerants, extensive investigations are in progress worldwide. This work reviews timeworn, current and the next-generation refrigerants using Refrigerant Qualitative Parametric (RQP) quantification model to assist the refrigerant choice decision process. It is based on the ratio of arithmetic sums of actual parametric values of refrigerants normalized to equivalent ideal values. This model can help in choosing alternative refrigerants to replace CFCs by HCFCs or HFCs provisionally and finally replacing HCFCs or HFC to low GWP and ODP synthetic and natural refrigerants. A set of 16 refrigerants, both natural and synthetic, as an example, is computed for the standard Vapour Compression Cycle (VCC) based on the proposed model using REFPROP (NIST- 23 standard). The techno-economic parametric values of chosen refrigerants are taken from cited literature, ASHREA safety standards and international environmental legislations, laws and protocols. This paper reports the environment benign natural (CO_2, NH_3, HCs) and a few synthetic (R-152a, R-1234yf) refrigerants to be the optimal options.

1. Introduction

The refrigerant is a substance or mixture, normally a fluid, used in heat cycle undergoing a reversible phase transition from a liquid to a gas and back. Refrigerators, air-conditioners, heat pumps, water heaters and many more devices use refrigerants as a mediating fluid to transfer heat between sources and sinks.

Refrigerants with suitable properties are chosen for selective cooling and heating applications [1]. Human society was using refrigeration technology, even before the invention of electricity in the 1880s. Historically, Oliver Evans (1805) pioneered the idea of refrigeration by using ether,. Jacob Perkin implemented this idea in his first refrigeration machine built in 1834. Later on, various researchers used petrol (1860s), NH_3 (1873), CO_2 (1886) and SO_2 (1890s) as mediating fluids in their refrigeration systems. From 1830 to 1930, ether, NH_3, CO_2, SO_2, H_20, CCl_4, $HCOOCH_3$, HCs, CHCs were the most popular refrigerants. Most of these refrigerants were toxic, flammable, and highly reactive and prone to accidents [2]. Midgley and Henne [3] invented the dichlorodifluorocarbon (CCl_2F_2) molecules in 1929, which were commercially produced as Chlorofluorocarbon (CFC-12) refrigerants by Dupont de Nemours in 1932 [4]. Widespread adoption of efficient CFC refrigerants in 1930s reduced the use of NH_3 and phased out CO_2 by 1950s. CFCs have been used for years as refrigerants, solvents and blowing agents by industry. Long journey of refrigerants from CO_2, NH_3 and HCs to HCFCs, HFCs and HFOs is once again ending up in mix of natural and synthetic refrigerants (CO_2, NH_3, HCs, HFO,R-152a, R-1234yf). There is no refrigerant in sight, which has all ideal properties [5]. A brief history of past, current and probable future natural refrigerants is shown in Fig. 1.

Early refrigeration history (1800) kick started with the use of natural refrigerants, which were replaced by synthetic refrigerants (1929) with superior thermal performance, safety, and durability. Some of the

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Nomenclature

P_E/p_C	Pressure ratio
pr	Reduced Pressure = p_{Conds}/p_{crit}
μ (μPa-s)	Dynamic Viscosity
h_{fg} (KJ/kg)	heat of vaporization
ķ(m-w/m-K	Thermal Conductivity
T (°C)	Temperature
P (bar)	Pressure
C°p (J- mol^{-1} k^{-1})	Specific heat at constant pressure
ρ (kg/m^3)	Dynamic Viscosity
p_{reduc}	p/p_{crit}, Reduced Pressure
P_r	Prandtl no.
p_{Cond}/p_{Evap}	pressure ratio
MROA (°C)	Maximum Range Of Applicability(T_{max})
M (kg/kmol)	Mass of refrigerants
COP	Coefficient of Performance
V_{SP}(m^3/kg)	Specific Volume
ω	Acentric factor
LFL	Lower Flammability Limit
p_{Cond}/p_{Evap}	pressure ratio
CR	Compression ratio p_{Conds}/p_{Evap}

Subscripts

FP	Freezing point
NBP	Normal boiling point (1.01 bar)
Evap	Evaporator
crit	Critical
v	vapour
n	normalized
red	Reduced pressure
IG	Auto ignition temperature
Conds	Condensor
l	liquid
a	actual

synthetic refrigerants, chlorofluorocarbons (CFCs) were noted to cause stratospheric ozone depletion, therefore, were banned under Montreal Protocol (1987). As a substitute, the hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) were proposed in 1980s. HCFCs were noted to cause ozone depletion and bear high global warming potential. Kyoto Protocol (1997) scheduled a phase out of HCFCs by 2020–2030 and HFCs by 2025–2040. Short-term permission to use HFC is an interim solution, not any justification. We are fast approaching the deadline, yet many countries are insolent, reluctant, and unaware or lack financial resources or technical know-how. This work reviews past, present and future outlook of refrigerants and assists the change decision process from high to low GWP and natural refrigerants for existing and future heating as well as cooling machines. An updated review on ozone depletion and global warming is also presented and current status is critically reviewed. Existing refrigerants are simulated for the standard Vapour Compression Cycle (VCC) based on the proposed model using REFPROP (NIST- 23) and original results are presented.

2. Natural refrigerants

Natural refrigerants occur in nature's chemical and biological cycles without human intervention. The natural refrigerants include ammonia (R-717), carbon dioxide (R-744), sulfur dioxide (R-764), water (R-718), air (R728) and ethyl ethers (R-610). Natural refrigerants were heart of HVACR industry from 1800s to 1930s until invention of high performance synthetic refrigerants. Rampant rise in synthetic refrigerants and fossil fuels started causing ozone depletion and global warming, which forced scientific communities and manufacturing industries saying goodbye to halogenated hydrocarbons in favor of natural refrigerants and fossil fuels in favor of sustainable and renewable energy technologies [8,9].

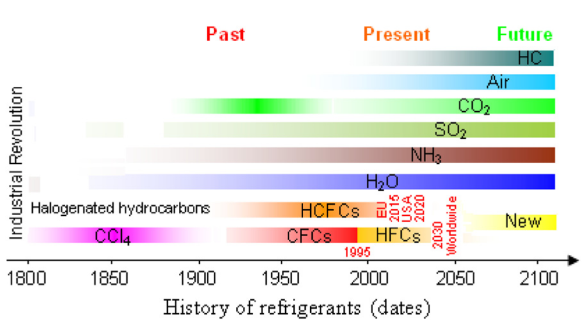

Fig. 1. A brief histogram of synthetic and natural refrigerants [6,7].

2.1. Water (R-718)

Water (R-718) is a non-toxic, non-flammable and abundantly available on planet earth everywhere. R-718 has high refrigeration effect as compared to CFCs, but requires ten times more volumetric flow for a given refrigeration capacity, this enhances the cost in the form of axial or centrifugal compressors [10,11]. Lee incorporated a simulation study using vapour R-718 as a refrigerant in a multi-stage compressor unit with inter-cooling strategy; he articulated that vapour R-718 has 30% higher COP compared to synthetic R-134a at full load. Kilicarslan et al. [12] presented a simulation based comparison between R-718 with R-290, R-717, R-134a, R-22 and R-152a for an evaporation temperature above 35 °C, and found R-718 exhibiting higher COP. Thermophysical properties of R-718 allow achieving COP, however, its high critical temperature (373.95 °C) and pressure (221 bar), high initial cost of axial or centrifugal compressors, high volumetric flow, large compression process, use of direct contact heat exchangers are limiting factors, rendering R-718 less attractive for heat pump applications [13].

2.2. Hydrocarbons (HCs)

Hydrocarbon (HCs) refrigerants include methane (R-50), ethane (R-170), propane (R-290), butane (R-600), isobutene (R-600a), ethylene (R-1150) and propylene (R-1270). HCs are ozone friendly and have a lower GWP as compared to HFCs. HCs offers excellent miscibility with synthetic oil, lower refrigerant charge and are compatible with the material of existing refrigeration and heat pump systems. Methane (R-50) and Ethane (R-170) are a flammable cryogenic liquid has an extremely low boiling point of − 162 °C and − 88.58 °C, respectively. These are used for extreme low temperature refrigeration (−80 °C). HCs such as propane appear, excellent candidates, to which researchers in contact with industry have reported safety issues [14]. R-290 and R-600 have similar characteristics as halogenated HCs but are flammable materials. R-290 has a higher cooling capacity than R-12 and similar COP when tested in propriety vapour compression refrigeration system [3]. The similar results were presented by B. Saleh and his fellow researchers using BACKBONE equation. R-1270 is an effective alternative of R-22 with higher capacity and COP [15,16]. Ignition temperatures of HCs are in the range of 420 °C (R-600) [17] to 600 °C (R-50) [18]. HCs have excellent environment friendly thermodynamic properties, but they are flammable. According to Missenden et al., a restricted amount of 200 g of HC refrigerant is recommended for domestic refrigeration systems whereas this amount does not exceed 0.40 g in such systems [19]. However Corberan et al. refereed to an amount of 150 g form a small sealed system in accordance with ISO, EU, IEC standards [16].