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Hydrocarbons and their mixtures as alternatives to environmental unfriendly halogenated refrigerants: An updated overview

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ABSTRACT

Vapor compression refrigeration systems consume high-grade energy and contribute to global warming and ozone layer depletion due to the environmentally unfriendly refrigerants. The use of hydrocarbons offer good drop-in replacements for the existing halogenated refrigerants in terms of environmental impacts and energy consumption. In this study, a review of the previous studies carried out with hydrocarbons as alternative refrigerants in refrigeration, air conditioning and heat pump, and automobile air conditioning systems is presented. An attempt has been made to cover the current status, possibilities, and problems related to the use of hydrocarbons as alternative refrigerants. Hydrocarbon characteristics, allowable refrigerant charge, flammable properties, and safety considerations are also presented. In addition, the study contains also a useful amount of information about the refrigerant properties, environmental impacts, and replacement strategy of conventional refrigerants. Results showed that in spite of highly flammable characteristics, hydrocarbons can offer proper alternatives to the halogenated refrigerants from the standpoint of environment impact, energy efficiency, COP, refrigerant mass, and compressor discharge temperatures. Roadmap on the future work needs in this field is presented. Finally, a summary of previous studies and strategies on pure HC, HC mixtures, and HC/HFC blends used for different applications has been presented and discussed in detail.

1. Introduction

Refrigeration plays a fundamental role in sustainable development since it has many applications in different number of fields in our daily lives. The most widely used refrigerators and air conditioning systems employ the traditional vapor compression refrigeration system (VCRS). However, the high-grade energy consumption of this equipment is very high and its working substances (refrigerant) create environmental problems that have to be solved urgently [1,2]. The VCRSs are responsible for about 30% of the total world energy consumption [3]. This amount can be increased when malfunction events occur in the system such as refrigerant leakage. Many attempts have been carried out to introduce the thermally driven cooling systems to overcome the problems associated with the VCRSs [4,6]. However, the low-energy efficiency prevents these systems from widespread utilization [7]. Therefore, the use of VCRSs will continue to expand worldwide especially in developing countries, due to its high COP [8].

Since the invention of the vapor compression cycle by Parkin in the 1830s, a large number of chemical substances had been tried and tested as a refrigerant. Chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are chemically synthetic substances commonly used as working fluids because of their excellent thermodynamic and chemical properties. On one hand, CFCs and HCFCs contain chlorine which reacts with ozone and destroys the atmospheric ozone layer. On the other hand, HFCs do not contain chlorine or bromine but they are greenhouse gasses that affect the global temperature of Earth's surface. Therefore all of these refrigerants contribute significantly to environmental impact and climate change. They have a global warming potential (GWP) higher than that of CO_2 (thousands of times) [9]. To fulfil global environmental issues effectively, all of these refrigerants has to be replaced by others with zero ozone depletion potential (ODP) and GWP. In addition, the performance of heat exchangers should be improved to minimize the indirect GWP caused by the electricity generated by the combustion of fossil fuels.

One alternative is to replace these halogenated refrigerants by the use of natural refrigerants, such as hydrocarbons (HCs). These HCs are naturally occurring, inexpensive, and can cover nearly every existing refrigeration application [10]. In addition, they have zero ODP and a very low GWP. More than that, hydrocarbons are not only just good for the environment but also, can be more efficient conductors of heat than halogenated refrigerants [11]. Hydrocarbons can be used in one of these forms; individual components (pure), blends of different hydrocarbons (HC mixtures) and components of blends containing halocar-

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bon refrigerants (HC/HFC blends) [12]. The main drawbacks of these substances are their potential flammability and other safety risks. However, such drawbacks may be disregarded for a minimal refrigerant charge, while safety precautions are considered and installed in large volume refrigeration equipment [13].

Several scenarios of hydrocarbons substitution are available in the literature. The first one is the drop-in, where the original refrigerant is removed from the system and replaced by another alternative refrigerant. Sometimes the process occurs with some minor modifications to the control settings of the equipment. The second one is the retrofit, where the original refrigerant is replaced with an alternative refrigerant often accompanied by oil and material changes due to compatibility issues. In both scenarios, the same main system performance may not be attained due to the use of the existing compressor and heat exchangers, except if the two refrigerants have similar properties. The latest scenario is the new system, replacement of original equipment with a new one designed specifically for the alternative refrigerant.

Following sections present the problems (environmental impacts and energy consumptions) associated with the use of halogenated refrigerants and the comprehensive studies related to the use of HC as an alternative in the VCRSs, the main objectives of the current study is to understand well the current status, possibilities, replacement strategy of conventional refrigerants, and problems associated with the use of hydrocarbons in the VCRSs. The study is organized into number of sections as shown in the contents.

2. Refrigerants and environmental impacts

2.1. Refrigerant properties

Refrigerant plays a vital role in the VCRSs since it is the medium by which cooling or heating is carried. Design, efficiency, and operating characteristics of a refrigerating equipment depend hardly on the different properties of the selected refrigerant. Thermodynamic properties of a refrigerant are essential for predicting the behavior of a system and the performance of its components. Excellent thermodynamic properties involve a boiling point somewhat below ambient temperatures, a critical temperature above ambient temperature, a high normal boiling point, and a high heat of vaporization. Good physical properties include; low specific heat capacity, low specific volume, and low viscosity, as well as high thermal conductivity. A refrigerant also must offer chemical stability under conditions of use in the presence of materials and lubricating oil and finally satisfy safety codes including non-flammability, non-corrosive, and non-toxicity [14].

Environmental properties comprise that refrigerant should not affect the ozone layer neither increase the GWP. In addition, cost, availability, efficiency, easy to handle and detect and compatibility with compressor lubricants and equipment materials are other issues [15]. It is a very long list of qualities and none of the current refrigerants can be considered as coming close to a perfect refrigerant adaptable to all applications. However, it is necessary to focus on selecting the right refrigerant for a particular application based on an overall assessment.

2.2. Environmental impacts

The halogenated refrigerants used in the cooling systems nowadays cause a threat to the environment when vented into the atmosphere because of their ODP and GWP.

2.2.1. Ozone depletion and global warming potential

The ozone gasses are found in the stratosphere layer, where it prevents the sun ultraviolet waves from arriving the Earth surface [16]. The molecule of ozone contains three oxygen atoms (O_3) and is unstable with respect to O_2. Ozone layer depletion has been associated with the presence of chlorine and bromine in the stratosphere layer as a result of the migration from chlorine containing chemical substances. The general agreement regarding ozone layer depletion is that free chlorine radicals remove ozone from the atmosphere, and later, chlorine atoms remain to change more ozone to oxygen [17]. A single atom of chlorine can destroy over 100,000 ozone molecules [18]. ODP of a substance is the relative amount of degradation it can cause to the ozone layer as compared to the influence of CFC-11 which is assigned a reference value of ODP=1.

The major source of the global warming is due to the increased volume of CO_2 and other greenhouse gasses in the atmosphere. These gasses act as a cover trapping heat and warming the planet. GWP is a measure of the amount of greenhouse gas (GHG) trapped in the atmospheric ambient compared to the effect of one kilogram of CO_2 over a specified time horizon. Therefore, ODP and GWP have become one of the most important criteria in analyzing new alternative refrigerants for the VCRSs.

2.2.2. Environmental impact of halogenated refrigerants

Halogenated refrigerants such as cfcs hcfcs and hfcs are chemical components obtained from hydrocarbons methane and ethane by replacing of chlorine and fluorine atoms in the place of hydrogen [19]. If hydrogen atoms are substituted in a halocarbon, it is fully halogenated. When halogenated refrigerants leak from an equipment during normal operating (filling, emptying) or accidental (damages), they gather in significant quantities in the stratosphere and participate to the breakdown of the ozone layer and GWP as mentioned before. Though the leakage is usually small, yet it is an important source of GHG emissions because of the high GWP of these refrigerants. In addition, refrigerant released from an equipment lead to insufficient system charge and negatively affect the performance of the equipment resulting in high energy consumption.

Table 1 shows the effect of different groups of refrigerants on the environment [20,21]. As observed from the table, CFCs and HCFCs show a high contribution to ozone layer depletion and the greenhouse effect, they have high ODP and GWP values. On the other hand, HFCs do not contain chlorine or bromine, their ODP values are negligible, but they show a serious greenhouse effect, extreme huge GWP values. Furthermore, natural substances such as HC have zero ODP and GWP.

2.3. Replacement strategy of halogenated refrigerants

The environmental impacts associated with halogenated refrigerants motivated scientists to investigate more environmentally friendly refrigerants. In September 1987, an international treaty called Montreal Protocol administered by the United Nations Environment Program (UNEP) was signed to control the consumption and production of refrigerants that deplete the ozone layer. Fig. 1 shows the phase-out plan of CFCs and HCFCs in developed and developing countries and use limitations on HFCs in the EU [9].

As a result of the Montreal protocol, the production of CFCs is completely phased out in developed countries by 1996 and 2010 in developing countries. CFCs then substituted by less harmful HCFCs refrigerants. HCFCs are planned to be phased out almost entirely by 2020, and totally by the end of 2030 in the developed countries and in 2040 in developing countries. Developed countries then started to use HFCs, that have no impact on the ozone layer but they still have high GWP. Proposals for the decrease of HFCs are also being discussed under the Montreal Protocol.

Countries have generally been aggressive and effective in implementing protocols and its subsequent amendments to slow and reverse the accumulation of stratospheric chlorine and bromine from ODS. Amendments and adjustments were agreed to in London (1990), Copenhagen (1992), Vienna (1995), Montréal (1997), and Beijing (1999), as shown in Fig. 2 [19]. These Protocols and modifications shortened the timetables for phasing out consumption of listed ozone-depleting substances.