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A REVIEW ON HYDROCARBON (HCs) AS AN ALTERNATIVE REFRIGERANT: BASED ON THERMODYNAMIC AND ENVIRONMENTAL APPROACH

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Abstract: This review paper present the possibilities of using hydrocarbons in the cooling and heating purposes in the vapor compression system are discussed elaborately. Different types of hydrocarbons (HC) as alternatives in terms of energy efficiency, exergy efficiency and heat transfer performance are analyzed. In developing countries, most of the vapor compression systems use halogenated refrigerants (HCFCs) due to their high thermal performance along with cost effectiveness. However, these refrigerants are harmful for the environmental belongings such as depletion of ozone layer and global warming. The search of alternative refrigerants is an ongoing process. This paper analyzes the different experimental and theoretical studies with HCs and their mixtures with HFCs and found that these are environmental friendly. It is concluded that some HCs, especially R600a and R290 are energy efficient and environmental friendly for the refrigeration and heat pumps. These also showed higher exergy efficiency compared to the other refrigerants like R134a, R12 and R22. REFPROP 7 software has been used to determine the thermophysical properties of the refrigerants.

Keywords: *Alternative refrigerant, Hydrocarbon, Exergy efficiency, Sustainable development.*

1. INTRODUCTION

Existing refrigerants have high ozone depletion potential and a significant role to warming up global when these are emitted directly into the atmosphere. Many researchers are involved in the research to search the alternative of the refrigerants with high efficiency and less environmental effect. The uses of natural fluids have appealed transformed interest during the last decade. Among the natural refrigerants, hydrocarbons have the potentiality to be the replacement of the existing refrigerants. Studies revealed that some of the HCs showed promising and interesting thermal and physical properties. HCs have the high latent heat of vaporization. So these are considered as an alternative to the existing refrigerants [1]. Vapor compression systems are widely used in many cases. It requires huge amount of energy and creates the less sustainable environment. Most of the energy is utilized for lighting, heating, cooling and air conditioning in our daily lifestyle. Which is one of the key source of energy utilization. The use of R134a is an alternative to unmodified R12 systems and heat pumps has been studied previously. Though R134a has acceptable energy efficiencies, it is expensive, highly hygroscopic in nature and global worming potential (GWP) 1700 [2-4]. Many of the researchers are believing that HCs can be easily adopted as an alternative refrigerant. They found to have the obvious advantages of being recognized as environmentally conscious and outstanding energy savings are also obtained. The only disadvantage of HCs is, its flammability that relative to other refrigerants. The flammability issue can be minimized by mixing HCs with a small amount of HFCs together for the commercial refrigeration where a large number of charges are essential [1]. The main objective of this study is to search proper hydrocarbon for the suitable vapor compression systems. Thermodynamic properties of the refrigerants were compared for different operating temperature. REFPROP 7 software has been used to determine thermal properties of the refrigerants. Authors studied not only based on first law analysis but also on second law analysis. Exergy destruction also is the key point for consideration as a refrigerant for the systems. Exergy analysis is

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typically intended to detect the maximum performance of any system. It also detects the sites of higher exergy destructions [5] among the whole system. Therefore, for selecting a refrigerant, it must be energy efficient, high exergetic, low cost, fewer environmental effects, compatible with all materials and chemically stable. This paper provides a complete criticism of the innumerable results carried out from the above-mentioned factors in freezers, air-conditioner, and heat pump applications.

2. BACKGROUND OF THIS STUDY

In the last few decades, refrigerants were selected based on thermodynamic performances for refrigeration. However these were poisonous or combustible or both. If there is a leakage in the refrigerators, it will cause a fire and become a health risk. In order to remove this risk, hermetically sealed motors were used. Except for air conditioning in the cars, all small and large compressors require hermetic motors to diminish the risk. Molina and Rowland [6] found that CFCs are mainly damaged by infrared contamination in the stratosphere. Chlorine atoms release in the stratosphere catalyzes the decay of ozone atoms to oxygen, are involves for global warming and hence regulations against the production and use of were in progress. Alternative refrigerants are found with CFCs improvement of the refrigerators/air conditioners having less ozone depletion and global warming potentials. HCFCs could meet the demand. Generally, R22 (HCFC 22) has been accepted as a suitable refrigerant for an air conditioner, refrigeration and heat pumps for a few decades. R134a (HFC) has been selected for refrigerator/freezer as a substitute of R-12 (CFC-12). R22 has an ozone depletion potential (ODP) of 0.5 and a GWP of 1600. However, R22 becomes a global phase-out because of its Global warming potential [7]. The replacement of R22 is an important issue for the air conditioner. Many works have been done to look for a suitable candidate of 22 during the last few decades. R134a has an ODP of zero while R22 GWP of 1200. It has been chosen in some countries for a refrigeration system for a short-term period. However, it has a lower performance than R12 and is not an environmentally advantageous refrigerant in terms of total equivalent warming impact (TEWI). In addition, lubricant for the compressor needs to be changed from mineral oil to synthetic oil [8]. At present, mixtures of HFC refrigerants such as R410A and R407C are being used in some of the countries instead of R22 [9]. Besides, many countries expend much effort to advance their individual substitute refrigerants for R22. Particularly, mixtures of refrigerants forming with environmentally safe pure refrigerants have expected a distinct consideration from the industries expecting a possible increase of energy-efficiency with the fluids. One of the probable solutions to escape HFCs is the use of hydrocarbons. The previous time, flammable hydrocarbons have been forbidden in general household refrigeration and air-conditioning applications due to the safety concern. These days, however, this trend is slightly relaxed because of an eco-friendly mandate. Therefore, some of the flammable refrigerants have been applied to certain applications [10–12]. Isobutane (R600a) has dominated the European refrigerator/freezer sector for the past decade and is being used even in Japan and Korea, while propane (R290) and propylene (R1270) are used for heat-pumping applications in Europe [13]. It is well known that HCs offer low cost, availability; compatibility with the conventional mineral oil, and environmental friendliness [10–11]. Furthermore, dimethyl ether (DME, RE1270) is a good eco-friendly refrigerant having excellent thermodynamic properties [14]. Nowadays, another miracle invention is Hydro-floro-Olefin as R1234yf used in the vehicles.

3. PROPERTIES OF REFRIGERANTS

3.1 Thermo-Physical Properties

Refrigerants should be non-toxic and non- flammable. Another thing is that it should have high thermodynamic performance (energy efficient) and low exergy losses. In practice, there is no such type of substance that could meet the entire requirement. Generally, a refrigerant is essential to fulfilling the requirements classified as thermodynamic, chemical and physical properties. The selection of any refrigerant for a particular application is directed mainly by the refrigeration capacity and its temperature such as for air conditioning (5^0C), cold storage (-10^0C to 2^0C), refrigerator (-25^0C), food freezing (-40^0C), etc. Thermodynamic properties are the main factor for choosing any refrigerant for a particular refrigeration system. Thermodynamic requirements belong to the evaporating and condensing pressures, critical temperature and pressure, freezing point, volumetric refrigeration capacity, COP, power consumption [15]. The critical temperature of refrigerant should be high so that the condenser temperature difference will remain very high from the critical point. For easy to evaporate, the boiling temperature of the refrigerant should be very low compared to the ambient condition. Lower discharge temperature of the compressor should be expected, which will save the compressor life.

Table 1 Thermodynamic properties of some common refrigerants

Refrigerant	Mol. mass	N. B. P. (^{0}C)	Critical temp. (^{0}C)	Latent heat (KJ/kg)	Freezing point (^{o}C)	Replaces
R-134a	102.03	-26.2	101.06	222.5	-96.6	R12
R-600a	58.13	-11.7	135.0	367.7	-159.6	R12, R134a
R-600	58.10	-0.5	153.0	385.6	-135	R12, R22
R-22	86.48	-40.8	96.02	233.2	-160	-
R-290	44.1	-42.1	96.8	424.3	-187.1	R12, R22
R407C	86.2	-43.6	87.3	257.75	-	R22
R410A	72.58	-51.5	72.5	273.18	-160	R22
R1270	42.08	-47.7	92.4	439.23	-184.44	R22

The freezing point of the alternative refrigerant should be lower than the system temperatures. The volume of suction vapor required for per ton of refrigeration also indicates the compressor size. Table summarized the thermal and chemical properties of pure and refrigerants blends. Physical properties of refrigerants are advantageous for determining the applicability of a refrigerant under design operating conditions. Thermodynamic and transport properties of refrigerants are required for expecting system nature and performance of machinery. Refrigerants which have high thermal conductivity, low viscosity in both liquid and vapor phases are desirable to archive a high-heat transfer coefficient with low power consumption. All the pure and mixed hydrocarbons have lower viscosity and higher thermal conductivity, which cause better performance of the condenser and evaporator. The thermophysical data for propane generally indicate somewhat better heat transfer coefficients in evaporation and in single-phase heat exchange than data for R22 [16–18]. Hydrocarbon refrigerants possess full chemical compatibility with nearly all lubricants generally used in the refrigeration systems. Good miscibility is maintained most lubricants under all operating conditions. Hydrocarbons are well soluble with mineral oils. Figure 1 displays the variation of the vapor pressure of the refrigerants with evaporator temperature. In this figure, R290 and R 1270 have very close vapor pressure to R22. R290 and R1270 can be used as a suitable alternative refrigerant to R22. Those two refrigerants are available in nature, cheaper and miscible with mineral oil (MO) and polyolester (POE) oil [13]. Even both are flammable in nature but could be acceptable for small uses. Another important thermodynamic characteristic of refrigerants is its latent heat of vaporization. Higher the latent heat of vaporization, higher heat transfer will occur during the boiling heat transfer process. Thus less amount of refrigerant will require cooling a room, which has a higher latent heat of vaporization.

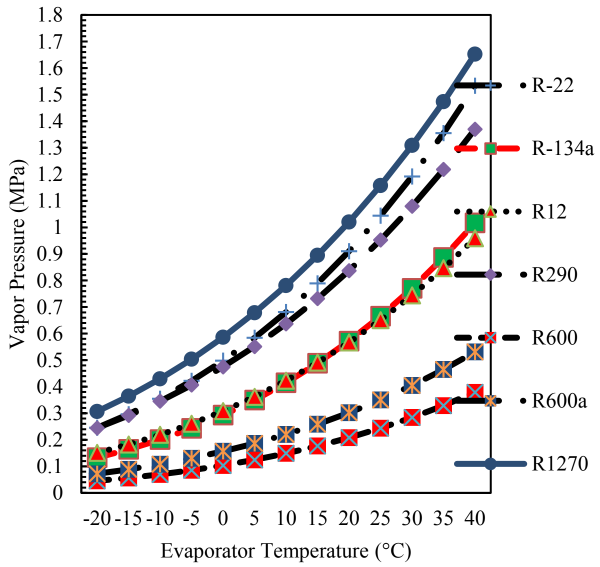

Fig. 1 Variation of the vapor pressure of different refrigerants with a different evaporation temperature.

Figure 2 presents the variation of the latent heat of vaporization of different refrigerants. From the figure, it is clear that hydrocarbon (HCs) refrigerants, R600, R600a, R290 and R1270 have the higher latent heat of vaporization then conventional refrigerants like R22, R134a, and R12. Thus, heat transfer will also increase while HCs are being used as an alternative instead of conventional refrigerants. Figure 3 shows the thermal conductivity of refrigerants for liquid and vapor phase. The thermal conductivity of the HCs refrigerants always greater than the conventional refrigerant. REFPROP 7 package software was used to determine all of the properties. Thermal conductivity is higher for R1270 and lower for R12 refrigerant, which makes hydrocarbon a suitable alternative to R22, R134a, and R12. The thermal conductivity is always higher at the liquid phase of the refrigerants. The heat transfer rate of refrigerants with higher thermal conductivity is more than the lower one. However, the thermal conductivity in the liquid phase is decreasing with the increment of temperature. Refrigerants, which have low viscosity in both liquid and vapor phases, are desirable to archive a high-heat transfer coefficient with low power consumption. Hydrocarbon refrigerants and its blend have the lower viscosity, which causes better performance of the condenser and evaporator. Figure 4 demonstrates the viscosity of different refrigerant for different evaporator temperature.

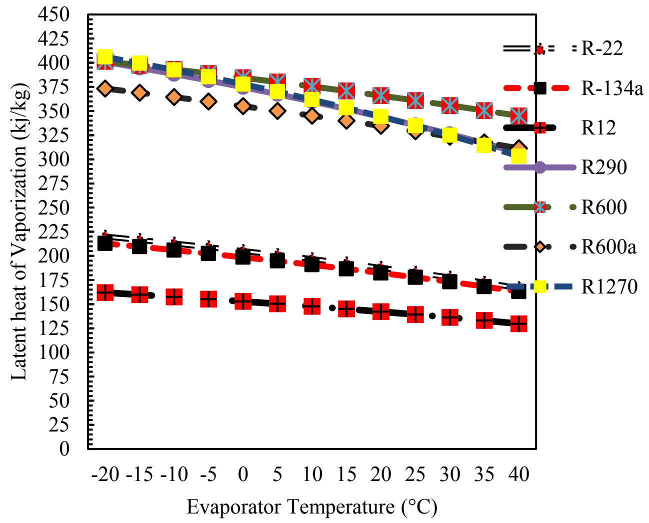

Fig. 2 Variation of latent heat of vaporization for different evaporator temperature.

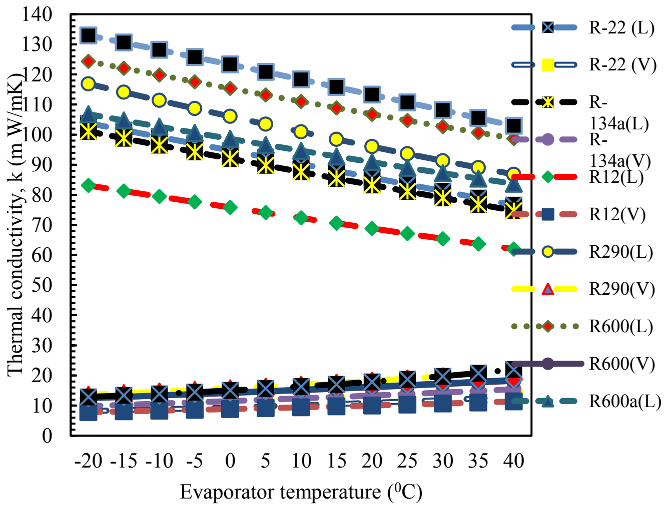

Fig. 3 Variation of thermal conductivity with evaporator temperature.

From the figure, it is clear that hydrocarbon refrigerants have lower viscosity comparing with R22, R134a, and R12. As the viscosity of hydrocarbon refrigerants is lower, it can be possible alternative refrigerants. R290 and R1270 have the lowest viscosity and can be used as an alternative to R22. Hydrocarbon mixture can be used as a refrigerant for better performance, but some of the refrigerants have different saturation pressures. It causes temperature glides in the evaporations. As per refrigeration manufacturer's recommendation, 3 K temperature variation in the evaporator can be permissible as mentioned by Sekhor *et al.* [20]. Miscibility test should also be done. Refrigerant should be miscible with the lubricant. Mohanraj *et al.* [21] found their mixtures (45.2% R290 and 54.8% R600a) were miscible with the lubricant and only 2.6 K temperature variation was occurred in the evaporator. Blends of HCs are the zeotropic substances, which have a greater possibility for development in energy efficiency and capacity accent. From thermodynamic characteristics analysis of different refrigerants, shown above, it concludes that hydrocarbons and its mixture can be a possible solution for future refrigeration and other processes.

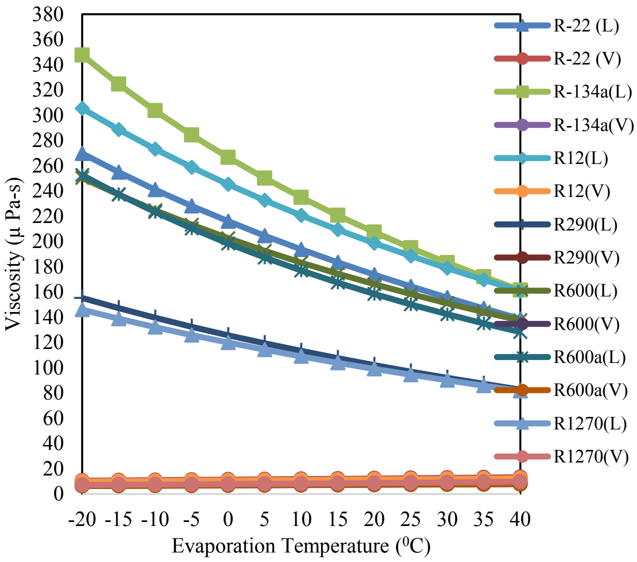

Fig. 4 Change of viscosity with evaporation temperature.

3.2 Environmental Considerations

Ozone in the Earth's stratosphere acts as a shield to prevent most of the damaging ultraviolet light from passing through the atmosphere. However, Rowland and Molina [6] discovered that CFC molecules were stable enough to remain in the atmosphere until they migrate to the stratosphere ozone layer. Then, the molecules will release a chlorine atom with the presence of ultraviolet radiation. Thus, the atomic chlorine will destroy the ozone layer. Consequently, the depletion of the ozone layer will allow more harmful ultraviolet reach the Earth's surface and cause genetic damage to living organisms. The Montreal Protocol [22] was called to find the solution for the ozone depletion. At the meeting, all the members agreed that the phase-out of CFCs will be by 2000. Moreover, at the 1992 meeting in Copenhagen, the participants of the protocol agreed to bring forward the phase-out date to 1996. Meanwhile, HCFCs are expected to be completely phased out by 2030. Ozone Depletion Potential (ODP) of a compound is the relative amount of the ozone degradation with trichloro-fluoromethane (R11) whose ODP is by definition. In recent times, considerable care has been paid to the natural fluids and are claimed to be more eco-friendly than the synthetic fluids [23–26].

Global warming is the phenomenon of an increase in the average temperature of the Earth's atmosphere and oceans in recent decades. The main cause of the scenario is the emission of greenhouse gases. Water vapor, carbon dioxide, and ozone are those major natural greenhouse gases. These natural fluids are HCs and their mixtures. These are suggested to be used as refrigerants in the household freezers to be replaced potentially with ozone-depleting fluids. These fluids have other advantages of being very inexpensive as well as available in anthropogenic greenhouse-gas emissions arise from fuel combustion and refrigerants. Undoubtedly, the CFC and HCFC contain high GWP. The global warming are responsible changes in the environment, including the rising sea level and the changes in climates. The highest GWP are hydrochlorofluorocarbons (HCFCs) those are found in refrigeration and cooling systems or HVAC-R equipment. All greenhouse gases are responsible for global warming potential values. This number is used by scientists to determine how gases, such as HFC, HCFC, and PFC refrigerants gases, will impact global warming within 20 years, 100 years, and 500 years. The values for hydrochlorofluorocarbons range from 120 to 12,240 over their atmospheric lifetime. When these numbers are broken down, it takes only one molecule of refrigerant gas to cause harm to the ozone layer. Table 2 shows the effect of refrigerants on global warming potential in the atmosphere.

Table 2 Global warming potential and ozone depletion potential of some refrigerants are used in the vapor compression refrigeration system.

No.	Code	Critical Pressure (MPa)	ODP	GWP
1	12	4.14	0.82	8100
2	134a	4.06	0	1300
3	50	4.638	0	20
4	170	4.891	0	20
5	290	4.25	0	20
6	600	3.8	0	20
7	600a	3.64	0	20
8	22	4.99	0.05	1810
9	407C	4.62	0	1530
10	410A	4.96	0	1730
11	1270	4.66	0	2

Source: ASHRAE Standard 34

Hydrocarbons are environmentally friendly with zero ozone depletion potential and do not cause any greenhouse warming effect. Sometimes some of the mixtures of hydrocarbons show less GWP. The standard equation for GWP (100) is derived on the basis of the ratio of time integrated radioactive forcing of 1 kg of a substance, relative to that of 1 kg of carbon dioxide over a 100 year time period [28–29].

$$GWP_X(TH) = \frac{\int_0^{TH} \Delta F_X dt}{\int_0^{TH} \Delta F dt} \quad (1)$$

Above methods to calculate the GWP is valid for sources of gas with long lifetimes. Mostly HFC are used as a refrigerant for their high thermodynamic performance. However, these refrigerants have high global warming potential (GWP) on the environment. GWP of R22 and R290 are found to be 1810 and 20 respectively in Table 2. But the mixture of 25% R290 with 75% of R22 shows GWP as 1355 using the Eq. 1.

4. EXPERIMENTAL AND THEORETICAL STUDIES FOR REPLACEMENT OF REFRIGERANTS

Numerous number of theoretical and experimental studies have been performed for pertaining to HC, HFC and their mixtures as alternatives to halogenated refrigerant for the different systems from the various parts of the world. Previously R12 was used as a refrigerant in the domestic refrigerator due to its high performance but for having high ODP and GWP R12 is phasing out now a days. Then R134a is used as a refrigerant. But due to its high GWP (1300) and being hygroscopic in nature it is also considered for replacement. Thus, researches are searching alternative refrigerant having zero ODP and minimum GWP. Tastoush *et al.* [30] tested with R600/R290/R134a in various quantities in the R12 domestic refrigerator. Authors reported that it is possible to use HC/HFC mixture as an alternative to R12 in the domestic refrigerator using mineral oil as a lubricant. The mass ratio of the mixture 25:25:30 and 80 gm charge showed very close performance to R12. Hammed and Alsaad [26] studied the performance of R12 based domestic refrigerator using R290:R600: R600a (50:38.3:11.7) as an alternative and found that the COP of the mixture is 3.7 whereas the COP of R12 is 3.6 (T_e=-16^0 C and T_c=27^{0}C). Wongwises and Chimres [31] inspected HC mixtures of R290 and R600 of different mass ratio to replace R134a. Their study reveals that, the mixture of R290 and R600 with mass ratio 60:40 shows the excellent thermodynamic and environmental properties compared to R134a. HC mixtures also show less energy consumption.

There are many research work performed by many scientists about HCs mixture as refrigerants [32]. Fatouh and Kafafy [33] experimentally analyzed the performance of R134a based domestic refrigerator with LPG composed of R290, R600a and R600 (by 60:20:20). The results showed that COP is increased by 7.6% and using capillary tube a significant charge (60 gm) is reduced. Akash and Said [34] studied the performance of the retrofitted system with LPG (30% R290, 55% R600 and 15%R600a) as an alternative at various charges (50g, 80g and100g). Results showed that 80 g mixture exhibits best thermodynamic performance and higher cooling capacities compared to that of R12. Jung *et al.* [35] examined R290/R600a as an alternative to R12 refrigerators. Results showed that for a mass fraction ranges from 0.2-0.6 of R290 causes an increase in COP up to 2.3% as compared to R12. Sekhor *et al.* [36] investigated that R134a/R290/R600a and R134a/9% HC mixture as the alternative to R12. The author found that energy consumption was reduced by 4-11% with 3-8% higher COP. Temperature glide in the evaporator is within 3 ^{0}C.

For industrial or large-scale refrigeration system needs more refrigerant charge. Thus the refrigerant provides high ODP and high GWP should be eliminated. Elefsen *et al.* [37] conducted a field test on R404 and R290 ice cream freezers in Australia. They reported that freezers using R290 consumes 9% less than that of R404 freezers. Spatz and Yana Motta [63] evaluated R404, R410, and R290 for replacing R22 in the medium temperature refrigeration system (walk-in cooler). The results suggested that R410A can be efficient and environmentally acceptable to replace R22 based on the life cycle climate performance analysis. Table 3 represent the alternative of the hydrocarbons as refrigerants studied by the researchers in recent time.

Table 3 Theoretical and experimental studies on HC refrigerant in the industrial and commercial sectors.

Authors	Refrigerant	Substitute	Findings
Peixoto *et al.* [38]	R134a	R600a	Energy consumption is reduced by 13% with the corresponding improvement in COP. Charge requirement of R600a is 50% of R134a.
Elefsen *et al.* [37]	R404A	R290	Freezers using R290 can operate satisfactorily and consumes 9% less energy than R404.
Spatz and Yana Motta [39]	R22	R404A, R410A, and R290	R410A showed to be efficient and ecologically acceptable in replacement of R22.
Sekhor and Lal [40]	R12	R134a and R290/R600a mixture	A mixture 9% HC blend (45% R290 and 55% R600a) showed the higher performance of 10-30% and 5-15% and less energy consumption in medium and low temperatures. It also showed lower outlet temperature and higher COP than those of R12.
Park and Jung [41]	R502	R1270 and R290, three mixtures of R1270, R290 and R152a	All the mixtures showed 9.6-18.7% higher capacity with 17.1 – 27.3% higher COP than those of R502. The charging requirement was reduced up to 60% as compared to R502.

Numerous researchers have been studied to select the best combination of HCs from the different refrigerants for air conditioners, heat pump, and chiller. Table 4 summarized the use of hydrocarbon refrigerant in the air conditioners and heat pump.

Table 4 Theoretical and experimental studies on HC refrigerant in the air conditioners, heat pump, and chillers

Authors	Refrigerant	Substitute	Sectors	Findings
Choi *et al.* [42]	R22	R32/R152a and R290/R600a	Residential heat pump	Based on the capacity, R32/R152a showed the best performance for having suitable glide matching in the HX. HC mixtures showed the highest COP with a loss in the system capacity
Purkayastha and Bansal [43]	R22	R290 and LPG	The heat pump of capacity 15kW	R290 and LPG mixture showed 18% and 12% higher COP than that of R22. Volumetric cooling capacities are lower by 16% and 14%, respectively.
Chang *et al.* [44]	R22	R290, R1270, R600, R600a, and binary mixtures of R290/R600a and R290/R600	Heat pump	Refrigerating capacity of R290 was smaller and COP was slightly higher than R22. The COP of R290/R600a with 50: 50 by mass was increased by 7% and R290/R600 at the composition of 75:25 showed 11% improvement.
Devotta *et al.* [45]	R22	R290	Window air conditioners	Cooling capacity was lower by 6.6-9.7%. Energy Consumption was by 12.4-13.5%. COP was higher by 2.8%-7.9%.
Devotta *et al.* [46]	R22	R407C	Window air conditioners	Cooling capacity was lower in the range of 2.1-7.9%. Power consumption was higher in the range of 6-7%. COP was lowered by 8.2-13.6%.
Jabaraj *et al.* [47]	R22	R123/R290	Chiller	Energy consumption was lower by 5-10.5% and COP was higher by 8-11% and refrigeration capacity was higher by 9.5-12.5%.

5. ANALYSIS BASED ON EFFICIENCIES

5.1 Energy Efficiency

Thermodynamic processes in a vapor compression refrigeration system release large quantities of heat to the environment. Conservation of energy is still the most commonly used method in the analysis of thermodynamic systems. Thermodynamic performance of the vapor compression refrigeration system is measured by the energy analysis for selecting the appropriate refrigerant. Now-a- days R134a is used for refrigerator and R22 is used for air conditioning system. But researchers are trying for high efficient, energy savings refrigerant as alternative. Due to high heat of vaporization, hydrocarbon shows high energy efficiency compared to other refrigerants. In 1996, isobutene R600a was used for the first time successfully in Germany, invigorated scientists to develop more green refrigerants for worldwide applications. Later, Richardson and Butterworth [48] used other refrigerants like R-290 and R-600a individually and tested their mixture in refrigerator. They used a vapor condensing system as test facility and found larger COP value than R-12. Lim *et al.* [49] first tried to experiment using mixed refrigerant of R-290 and R-600a as a replacement of R-12 for domestic refrigerators. They concluded that refrigerating effect was improved and total energy usage was saved about 3%. Also, a popular scientific magazine ‘‘hydrocarbon technology” in 1996 presented the comparisons of using R-600a, mixture of R-290 and R-600a, and R-134a as a substitute of R-12 in domestic refrigerators elaborately and showed 8.5% higher COP while using R-600a instead of R12. They also found that R-290/R 600a refrigerant has over 200% higher refrigerating effect than R-12 and approximately double refrigerating effect than R-134a.The improved energy efficiency of hydrocarbon refrigerants has been confirmed in the individual test and trails. Many researchers found that hydrocarbons are the best refrigerant compared to the other refrigerants. Table 5 shows their summarized study.

Table 5 Replacement of Hydrocarbon as refrigerant on the basis energy efficiency

Refrigerants	Authors	Results
R22, R290, R1270, Care 40 and 50	Pellitier and Palm [19]	All tested HCs showed better heat transfer in the evaporator compared to R22
R12, R600a	Kim *et al.* [8]	COP of R600a is 6% greater than R12. Energy savings with R600a is achieved by 1~11% compared to R12.
R134a, R600a and R290 blend, R12	Sekhor et. al. [36]	The HC blend with R134a showed better performance than R12, results 28.6% less energy consumption and enhancement in COP was 6-10%.
R134a, R290, R290/R600, R290/R600/R600a, R290/R600/R134a, R290/R600a/R134a	Wongwises S, and Chimres N. [31]	The mixture of R134a among each group is the best alternative.
R22, R407C and R410A	Kim *et al.* [50]	The mass flow rates of R407C are greater by 4.0%, and those of R410A are greater by 23% as an average, than those of R22.

5.2 Exergetic Analysis

Based on the first law of thermodynamics, energy performance of the HVAC systems is generally calculated. While, comparing with the energy analysis, the exergy analysis is capable to show accurately the sites of inefficiencies. This is a relatively new practice in which the basis of evaluating the thermodynamic losses monitors the second law rather than the first law of thermodynamics. The results from exergy analysis can be used to judge and enhance the performance of the HVAC systems. Saidur *et al.* [51] has found that major exergy losses are occurred in the refrigerator –freezer. Their studies indicate that a major part of exergy losses in the energy sector is affected for the vapor compressor system (Refrigerator and air conditioner, 33%).Their results summarized that it is necessary to reduce the exergy losses in the vapor compressor sectors to achieve the improvement. Using the concept of irreversibility, it is more supportive in defining the optimum operating conditions [52]. In addition, integration of energy, entropy and exergy analysis are able to present a whole picture of the system performance. Nowadays, it is suggested that propane/butane can be used as refrigerant instead of HFC134a. There are a number of explanations in this issue. Firstly, the refrigerator in the experiment using propane/butane as refrigerants requires less energy than the refrigerator uses R134a. This is due to having lower saturation temperature and higher latent heat of vaporization of propane/butane than those of R 134a. Hence exergy destructions are lowered. On the basis of second law efficiency, hydrocarbons are appropriate refrigerants. Alsaad and Hammad [25] examined the performance of a domestic refrigerator using R290/R600 mixture for a potential replacement of R12. A comparative analysis is offered for different pure HCs like R290, R600, R600a, R1270 and also R22 as well as R134a with theoretical analysis. This was a relative study considering energetic and exergy performance [53]. The energetic and exergy efficiencies reach at the maximum values for R1270 at all working conditions. However, the similar efficiencies were obtained with R600.

Using a developed computational model [54], coefficient of performance (COP), exergy destruction (ED) and exergy efficiency of refrigerants R-22, R-407C and R-410A were predicted. These investigations were carried out for evaporator and condenser temperatures within the range of -38^0 C to 7^{0}C and 40^{0}C to 60^{0}C, respectively. The results indicated that COP and exergy efficiency for R-22 were higher than those of R-407C and R-410A. The optimum temperature in the evaporator with minimum ED ratio has been evaluated at different condenser temperatures. Experimental study of Aprea and Greco [55] showed that R-407 is not an alternative of R-22 for air conditioning system. Kilicarslan and Hosoz [56] investigated the energy and irreversibility parameters of a cascade refrigeration system employing different refrigerant couples, namely R152a-R23, R290-R23, R507-R23, R234a-R23, R717-R23 and R404a-R23. In all cases, the refrigerant couple R717a-R23 showed the highest COP and lowest irreversibility. Though there are some limitations in the case of using the natural refrigerants, the couple R152a-R23 is the solution. Venkataramanamurthy and Kumar [64] investigated the energy, exergy flow and 2nd law efficiency of vapor compression refrigeration system using R22 and R436b. Exergy efficiency and COP of R436b (58% of R290, 42% of R600a) were found higher than that of R22 in all the ranges of temperatures. Another thing is that R 436b has low GWP (3) and zero ODP. An exergy analysis was conducted for a domestic refrigerator between the evaporation and condensation temperatures ranges from -15^{0}C and 40^{0}C by using R12 and R413 refrigerants [65]. Authors found that the overall exergy performance of R413a is better working with R12. System working with R413a required less power consumption and less irreversibility. Table 6 shows an overview on exergy analysis based on hydrocarbon refrigerants and its blends. It is apparent to conclude from the above discussion that, hydrocarbon (HCs) is a very suitable alternative based on exergetic point of view.

Table 6 Effect of refrigerant on exergy loses for a vapor compression system.

Objectives	Refrigerants	Reference	Findings
Exergy Analysis	R22 and R407	[57]	Irreversibly in the compressor is high.
Theoretical Analysis of vapor compression system	R 502, R404 and R507	[58]	Exergy efficiency of R507 is better compared to the other refrigerants
Energy and energy analysis of pure hydrocarbons	R290, R600, R600a, R1270 , R22 and R134a	[59]	R1270 showed better energy and exergy efficiency, R600 also same efficiency
Thermodynamic analysis of vapor compression analysis	R134a, R12, R502	[60]	R 134a showed better performance on the basis of 2nd law efficiency and interstaging is better than single staging
To find the COP, exergetic efficiency and exergy destruction	R-22, R-407C and R-410A	. [61]	COP and exergetic efficiency of R22 is higher compared to others
Exergy based Refrigerant selection	Three mixtures: R23/R290,R23/R600,R125/R600	[62]	Less exergy loss with R23/R290 in comparison with R125/R600 and R23/R600 mixtures
Exergy and energy analysis of a split type air conditioner	R-22, R600a	[63]	Exergy destruction reduced significantly. Exergy efficiency increased.

6. FLAMMABILITY AND SAFETY CONSIDERATION

Any refrigerant that will be used as alternative solution to HCFC refrigerants, must be occupied with excellent attributes of HCFC. From the thermodynamic and environmental consideration, it can be easily referred that hydrocarbon (HC) based refrigerants (like as R600, R600a, R290 and LPG) have almost similar properties of R134a, R22, R12 and other HCFC refrigerants. In many cases, HC showed improved thermal behavior than that of HCFC. But the implication of HC refrigerants in refrigeration and air-conditioning systems were prohibited due to their inherent flammability property. ASHRAE Standard 34 classifies the refrigerants into categorized based on their toxicity (A or B) and flammability characteristics (1, 2 or 3) as shown in Table 7 [66]. Flammability limits are interpreted as the range of concentration in which a flammable object can initiate fire or explosion when disclosed to an ignition medium [67]. Flammability limits are categorized into two groups: (i) Upper Flammable Limit (UFL) above which the substance concentration is too rich (deficient in oxygen) to burn; (ii) Lower Flammability Limit (LFL) below which the fuel concentration becomes too lean (sufficient in oxygen) to be ignited. Between the UFL and LFL lies the flammable area where the mixture will easily to ignite when given a source of ignition. Hydrocarbon is a low toxic and high flammable refrigerants (A3). Some attributes in relation to the flammability and ignitions data compatible to HC refrigerants are reported in Table 8 [68,69].

Table 7 Safety classification of refrigerants

Flammability	Safety Group	
	Lower Toxicity	Higher Toxicity
Higher	A_3	B_3
Lower	A_2	B_2
Non-flame	A_1	B_1

Table 8 Flammability properties of Hydrocarbon refrigerants.

Refrigerant no.	LFL (%)	UFL (%)	Auto-Ignition temp (°C)	Ignition energy (J)
R290	2.1	9.5	466	0.00025
R600	1.6	8.4	420	0.00025
R600a	1.8	9.6	462	0.00025
R170	3	12	515	0.00024
R1270	2.5	10.1	455	0.00028

The safety measures to be taken are established on the charge quantity of refrigerant, meaningful modifications in system design, and physical location of the unit [70]. To minimize risk associated with HC refrigerants, following recommendations must be taken into account [71]:

- Confining the hydrocarbon in a closed system or reducing the number connections.
- Restricting the maximum amount of hydrocarbon is charged.
- Providing adequate ventilation system to narrow the concentration of HC in the ambient air lower than the flammability limit.
- Removing the source of ignition associated with the system.

Considering safety issues it is viable to develop potential systems with equivalent efficiencies, or even higher than, those of CFCs, HCFCs and HFCs systems [72]. It should be kept in mind that millions of tons of hydrocarbon substances are used safely over the world for cooking, heating, powering vehicles, aerosol propellants and etc.

7. IMPROVEMENT USING NANOPARTICLES

Some researchers found that some additives with high conductivity enhance the heat transfer rate. So, a small amount of refrigerant is necessary for creating same refrigerating effect. Due to decrease in mass flow rate exergy loss also decrease. In the other hand for the same refrigerant flow, the difference in the operating temperatures will be reduced. Thus clearly this temperature reduction will cause to reduce the exergy losses in the whole systems. Sometimes this addition is called nano fluids. Nanofluids are a relatively new class of fluids which consist of a base fluid with nano-sized particles (1–100 nm) suspended within them [73,74]. These particles, generally a metal or metal oxide, increase conduction and convection coefficients, allowing for more heat transfer out of the coolant [75–77]. In the literature, a number of reviews on heat transfer using different nanoparticles are investigated by many researchers [78–79]. Copper Oxides (*CuO*), carbon nanotubes helps to enhance heat transfer. In the field of lubrication, it has been reported that a carbon nanolubricant might substantially reduce the frictional coefficient with respect to pure oil, which means a better lubricating operation for scroll compressor [80]. Kedzierski and Gong [81] found that a lubricant based nanofluid (nanolubricant) made with a synthetic ester and CuO particles caused a heat transfer enhancement relative to the heat transfer of pure R134a/polyolester (99.5/0.5) of between 50% and 275%.Eastman *et al.* [82] found that thermal conductivity of 0.3% copper nanoparticles of ethylene glycol nanofluids is increased up to 40% compared to that of the base fluid. Authors stressed that, this property plays an important role in construction of energy efficient heat transfer equipment. Liu *et al.* [83] investigated the thermal conductivity of copper–water nanofluids produced by chemical reduction method. Results showed 23.8% improvement at 0.1% volume fraction of copper particles.

8. CONCLUSIONS

The present demonstration provides an encyclopedic review of the various studies pertient to hydrocarbons as alternative refrigerants in refrigeration, air conditioning and heat pump, and automobile air conditioning systems. A number of hydrocarbons have suitable characteristics as the refrigerant from the thermodynamic, thermo-physical, exergetic as well as heat transfer point of view. All the hydrocarbons have excellent environmental characteristics, zero ODP and negligible GWP. The hydrocarbons R290 and R600a show better performance on the basis of energy, exergy and heat transfer for the domestic refrigerators. Based on the outcomes found on different studies and the previous summary relevant to hydrocarbons the following points can be drawn:

i) The thermodynamic and thermo-physical properties of HC is convenient to the traditional refrigerants.
ii) The application of hydrocarbons as an alternative to the existing HCFC refrigerants are not only good for the environment but also it can minimize the energy consumption.
iii) Hydrocarbons offer interesting behavior as alternatives for conventional ones from the viewpoint of energy efficiency, COP, refrigerant charges, and compressor's discharge-temperatures.
iv) The blends of HC/HFC mixtures can be used to restore CFC and HCFC offering same life-time as the existing systems.
v) As hydrocarbons are flammable, most of the researchers used low refrigerant charge in large capacity systems.

vi) R290 has been successfully commercialized to replace R22 in low charge, room and portable air conditioner. HC mixtures such as R432A and R433A and HC/HFC mixtures (like R470c/R600a/ R290) are accepted as an environment-friendly option for replacing R22 in air conditioning and heat pump applications.

vii) HC and HFC/HC mixtures are found to be the good substitutes for replacing R12 and R134a in domestic and commercial refrigeration systems.

The present study introduce the idea behind the search of alternative refrigerants to HCFC. The information provided in the article can be used to carry new research related to hydrocarbons and their blends as an alternative to CFC and HCFC.

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