A Review of an Alternative to R134a Refrigerant in Refrigerators

Mohammed F. Mohammed, Maathe Abdulwahed Theeb

Mechanical Engineering, University of Mustansiriyah, Baghdad, Iraq
Email: ehma013@uomustansiriyah.edu.iq

For several decades, the use of refrigerants has been developed in refrigeration cycles, especially in refrigerators, and these developments have increased due to the urgent need for them with regard to preserving the environment and the ozone layer, and protecting the earth from global warming, in addition to improving the efficiency of the cycle. Many refrigerants were used, including hydrocarbons and hydrofluorocarbons, especially R134a, the most prevalent, and then the trend was to reduce its use to damage the ozone layer, and its damage to humans as well. The available alternatives to R134a from refrigerants as well as from refrigerant mixtures were reviewed, in addition to their physical and chemical properties.

Keywords: R134A, alternatives, refrigerator, refrigeration cycle, ODP, GWP.

1. Introduction

The main idea on the basis of which refrigerators were used for the purpose of cooling is the process of transferring heat from a closed space with a low temperature to the outside environment with a higher temperature[1]. There are many methods that are used for this purpose, but the most used method is a single-stage vapor compression refrigeration system (VCRS). Fig. 1 shows the diagram of refrigerator[2]. The vapor compression systems are responsible for about 30% of the entire energy consumption in developed countries[3]. Each of these terms used has its own physical and chemical properties that achieve a certain acceptability within use, such as the impact on humans and the environment in addition to prices.

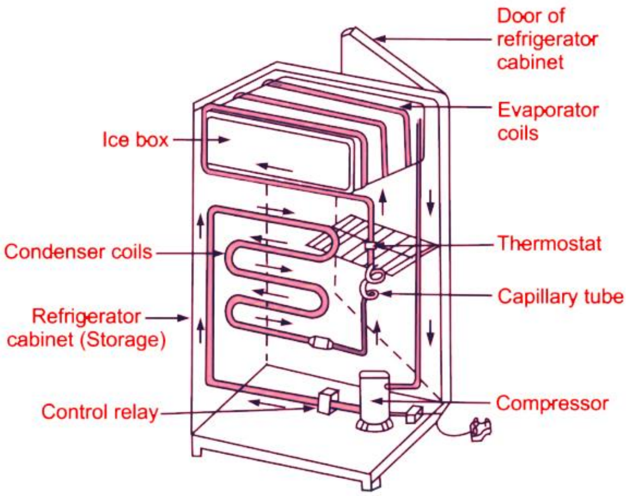

Figure 1 Diagram of household refrigerator

These refrigerants are being developed on a wide range in accordance with global trends aimed at preserving the environment, especially the protection of the ozone layer, in addition to preserving the earth from global warming, which causes an unacceptable rise in earth's surface temperatures[4] [5]. The chemical components of the refrigerants determine the nature of the negative impact of the refrigerant on the environment. This means that the fluorescent content in certain proportions may be responsible for the phenomenon of global warming, and chlorine levels are also responsible for destroying the ozone layer [6][7].

One of the most common refrigerants is R134a, which is widely used in domestic refrigeration systems at medium temperatures, but the problem with its use is that this refrigerant has the ability to cause global warming, with a global warming capacity of approximately 1430[8][9][10]; Therefore, the global trend was towards reducing its use, and even using alternatives that fulfil the desired requirements. Including the Montreal Protocol 2010, in which it was decided to gradually reduce the use of CFC refrigerants[11]. One of the most dangerous factors affecting the use of refrigerants is flammability, and it is worth noting that R134a one of its disadvantages is its flammability if mix with air under pressure then exposed to a strong ignition source. For these and other reasons, it has become necessary to use alternative refrigerants and mixtures to R134a in order to achieve the desired requirements. Refrigerant replacement processes went through several stages, including replacing CFC refrigerants with HCFCs and then with HFCs that contain zero ODP[12]. Fig. 2 shows the GWP values of some R134a alternatives.

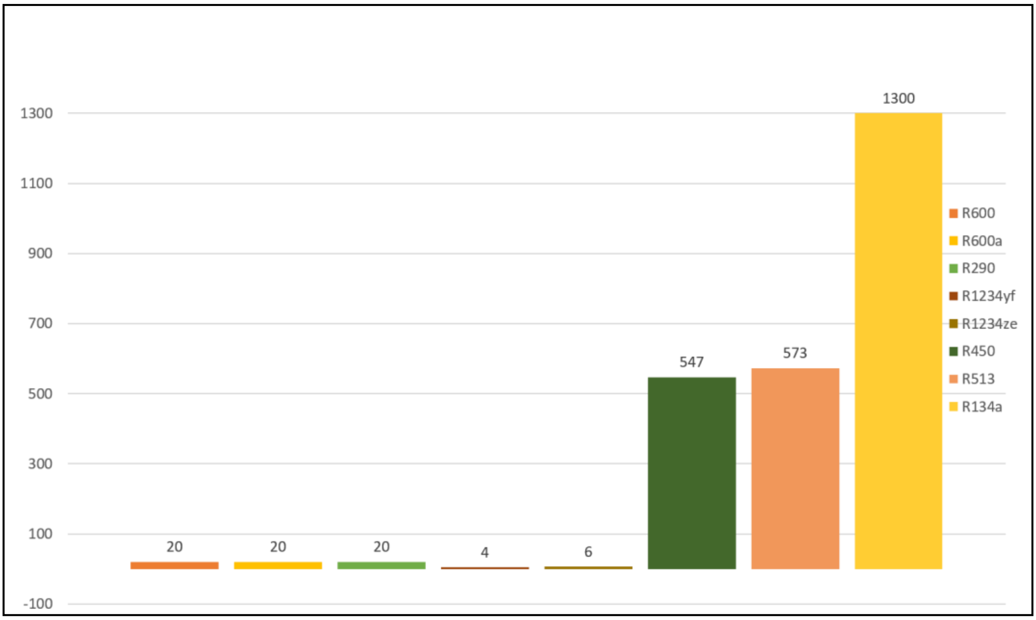

Figure 2 GWP of some R134a alternatives

2. Types of Refrigerants

Generally, refrigerants can be classified into two main types, pure refrigerants, and mixtures. As for pure refrigerants, they are divided into synthetic refrigerants and natural refrigerants, while mixtures are of two types: azeotropic and zeotropic. Fig. 3 shows types of refrigerants.

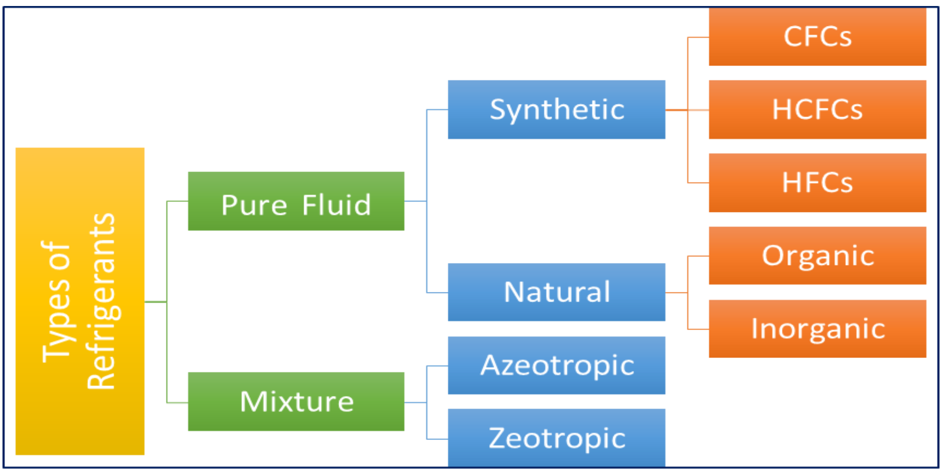

Figure 3 Types of refrigerants

2.1 Pure Refrigerants

Pure refrigerants are refrigerant that have an evaporation temperature that is a function of saturation pressure and remains constant throughout the refrigeration cycle[13]. These refrigerants consist of two parts, synthetic and natural refrigerants[14].

2.1.1 Synthetic Refrigerants

The discovery of these refrigerants led to the acceleration of industrial development and the comfort of mankind, on the other hand, climatic changes, including ODP are the main disadvantages. Standard synthetic refrigerants, such as HFC, HFO, and CFCs, were widely replaced by HFC (R-134a) and HCFs. HFCs do not cause global warming, but when exposure to UV in the troposphere, they can breakdown into acid and toxic chemicals, which eventually rain down[14].

2.1.2 Natural Refrigerants

Without human involvement, natural refrigerants take place in chemical and biological natural processes. Ammonia, carbon dioxide, sulfur dioxide, water, and air are examples of natural refrigerants [15]. These refrigerants were the backbone of the HVACR business for more than century, when high-performance synthetic refrigerants were invented. Ozone depletion and global warming were caused by a rapid increase in man-made refrigerants and fossil fuels, forcing scientific societies and industrial trades to abandon halogenated hydrocarbons for the benefit of natural refrigerants and fossil fuels for the benefit of sustainable and renewable energy technologies[14][16].

2.2 Refrigerant Mixtures

It consists of two or more refrigerants and is divided into two types:

2.2.1 Azeotropic

Azeotropic refrigerant mixtures (ARMs) are multi-components that do not change composition when they evaporate or condense at the azeotropic point because both components have the same boiling temperature at that composition and pressure. It consists of two or more different kinds of molecules. In reality, an ARM only behaves this way at a single temperature and pressure. Deviations from this pattern in other locations are minor and hardly imperceptible.

2.2.2 Zeotropic

Zeotropic : A zeotrope is a working fluid that has two or more components with distinct vapor pressures and boiling temperatures, and when the fluid evaporates or condenses, the liquid and vapor components have different positions. It's made up of two or more different kinds of molecules. The evaporation and condensing temperatures alter with composition under constant pressure. Glide is the term for the temperature shift that occurs during a constant pressure phase transition. It varies according on the components utilized and their quantities. (For more information, see Temperature Glide.) The degree of glide displayed by a zeotrope is a measure of how far it has strayed from being an azeotrope. Azeotropes have zero glide at their azeotropic point by definition. They may, however, glide under certain circumstances[17].

3. Properties of R134a

R134a has several characteristics that have made it so widespread [18] [19]. Table 1 shows some properties of R134a.

Table 1 Properties of R134a

Refrigerant	R134a
Composition	pure
ASHRAE safety classification	A1
ODP	0
GWP100-yr (AR5, Myhre et al., 2013)	1300
Critical temperature (ºC)	101.1
Critical pressure (kPa)	4059.3
NBP (ºC)	-26.4
Glide (ºC) at 100kPa	0
Liquid density a (kg m-3)	1295.3
Vapor density a (kg m-3)	14.35
Liquid cp a (kJ kg-1 ºC-1)	1.341
Vapor cp a (kJ kg-1 ºC -1)	0.897
Liquid thermal conductivity a (W m-1 ºC -1)	92.08
Vapor thermal conductivity a (W m-1 ºC -1)	11.50
Liquid viscosity a (Pa s-1)	267.0
Vapor viscosity a (Pa s-1)	10.7

Source: [18],[19]

3.1 Drop-in Refrigerants to R134a

The term "drop-in" is used in refrigeration operations to express the use of refrigerant substitutes without the need to add or modify other equipment [20]. Fig. 4 below shows a general view of R134a alternatives. Table 2 shows some properties of some refrigerants.

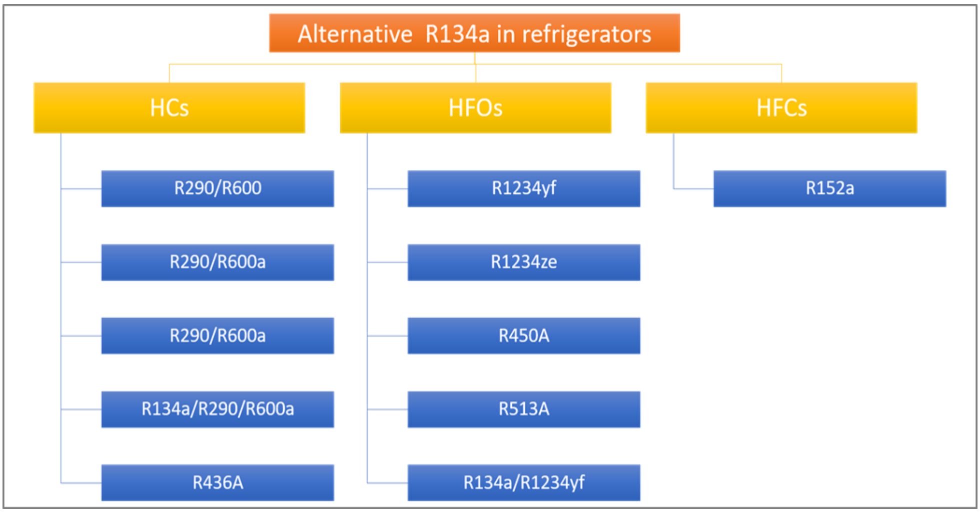

Figure 4 General view of R134a alternatives

4. Literature review

4.1 Hydrocarbons (HCs)

Hydrocarbons are one of the most fundamental materials on the planet. They are made completely of hydrogen and carbon. Hydrocarbons can be utilized as refrigerants in the refrigeration and air conditioning industry. Propane (R-290), isobutane (R-600a), and propylene (R-1270) are some of the most regularly utilized hydrocarbon refrigerants. One of the most important advantages of hydrocarbons is the thermodynamic properties that allow it to be used as a drop substitute in refrigeration systems, as it has the ability to mix with synthetic lubricants [21].

It is worth to be mentioned that for a variety of reasons, hydrocarbons (HCs) are excellent refrigerants, copper and ordinary mineral oils are compatible with them. In compared to CFCs, HCFCs, and HFCs, they have a relatively minimal environmental effect. They deliver excellent results, with high capacity and efficiency. Due to lower liquid densities and smaller refrigerant charge than HFCs, the heat transfer coefficients are higher, resulting in a higher latent heat of vaporization. In comparison to HFCs, HCFCs, and CFCs, the system's coefficient of performance (COP) improves and power consumption decreases with HCs; the compressor's life is extended due to the lower discharge temperature[22].

4.1.1 Pure Hydrocarbons As A Drop-In Refrigerants

Borneni and Satyanarayana [23] in their experimental study used a domestic refrigerator with a capacity of 165L and calculated its COP when using R134a and R600a, also when using an internal heat exchanger, their study showed that COP improved by using R600a, using heat exchanger improved the performance of the refrigerator 0.95. Similarly, while 10% reduction in compressor discharge temperature by utilizing a heat exchanger, the energy consumption of the refrigerator progressively increased by 3% when compared to a standard household refrigerator. Also Qureshi and Bhatt [24] agreed with the findings of Boorneni and

Satyanarayana [23], they used R600a (50g) domestic refrigerator, which has 66% lower refrigerant mass, higher COP, higher cooling capacity and lower energy consumption compared to R134a.

Another comparative analysis for using R600a as substitute refrigerant to R134a in a household refrigerator [25], Since the latent heat of hydrocarbon is substantially greater than that of R134a [26], the experiment was conducted using a 100-g charge of R134a according to the refrigerator manufacturer's specifications versus a 50-g charge of R600a refrigerant in the system. it showed that the COP achieved with R600a is greater than that obtained with R134a.

Additional investigation [27], in which R600a was employed as a substitute for 145 g of R134a in a residential refrigerator, confirmed the earlier findings. R600a requires only 50 g of charge, which is 66 percent less than R134a. To improve system performance, the study advised that the compressor be heavily modified.

On the other hand, a study [28] employed propane in their research and discovered that cooling efficiency and COP were 40.5–67.4 percent and 2.8-22.4 percent greater than those of R134a, respectively. The compressor's electric power consumption increased by 44.8 percent, necessitating the usage of a larger compressor than in the case of R134a. Due to its low COP and higher working pressures, R290 has been regarded as unsuitable for using as a direct drop-in substitute for R134a in residential refrigerators.

4.1.2 HC Blends and HFC/HC Blends

An experimental investigation [26] claimed that the use a blend of propane and isobutane (45.2:54.8 mass ratio) in a 200 liter domestic refrigerator for a wide outdoor temperature range between 24 and 43 °C reduced pull-down time, ON time ratio, and hydrocarbon mixture energy consumption by about 11.6 percent, 13.2 percent, and 11.1 percent, respectively. The trials revealed that 45 percent of the HC mixture was removed from the charge requirement. Furthermore, because the hydrocarbon mixture used less energy to drive the compressor, the environmental implications were lower than those of R134a.

In addition, Kathar and Surushe conducted an experimental study to evaluate the act of a 220 liter home refrigerator using a blend of propane and isobutene for equal proportion instead of R134a. The new blend charge was about 50 percent. The cooling efficiency was larger than 35.29 percent and 12.5 percent. The compressor operated decreased by 9.12 percent and 14.68 percent. COP was larger by 46.92 percent and 31.91 percent, and the temperature of compressor discharge was lower by 8 K and 5 K with respect to R134a, respectively.

Also, Kathar and Surushe [29] conducted an experimental investigation to evaluate the performance of a 220-litre home refrigerator employing (R290/R600a, 50:50 by weight) to replace R134a. The refrigerant mass charge of R290/R600a was nearly 50%, with refrigeration effect higher by 35.29 percent and 12.5 percent, compressor operate lower by 9.12 percent and 14.68 percent, COP larger by 46.92 percent and 31.91 percent, and discharge compressor temperature lower by 8K and 5K than R134a, respectively.

As theoretical study[30] for using propane/commercial butane mixture as alternative refrigerant for R134a found that under normal, subtropical, and tropical operating conditions, the propane/iso-butane/n-butane mixture with 60% propane is the optimum drop-in substitute for R134a in household refrigerators. The pressure ratio of the hydrocarbon mixture containing 50%, 60%, and 70% propane is about 6.3 percent, 11.1 percent, and 15.3 percent lower than that of R134a, respectively. The compressor input power requirements for R134a and the ternary hydrocarbon blend of 60% propane are practically identical. The volumetric cooling capabilities of the hydrocarbon mixture with 70% propane are almost 15.5 percent greater than those of R134a. However, R134a and R404a have different volumetric cooling capabilities.

4.2 Hydrofluoroolefins (HFOs)

4.2.1 Pure HFOs as alternative of R134a

Unsaturated organic molecules composed mainly of hydrogen, fluorine, and carbon are known as HFOs. As refrigerants, these organofluorine compounds are of interest. HFO refrigerants have zero ozone depletion potential (ODP) and a low global warming potential (GWP) of less than 6, making them a more environmentally friendly option than CFC, HCFC, and HFC refrigerants, but it is more expensive than R134a. HFOs have shorter tropospheric lives than HCFCs and HFCs [31][32]. Because of the double carbon bond in the molecule, HFOs breakdown quickly in the lower atmosphere, resulting in a low GWP but also flammability[33]. R1234yf is the most common refrigerant in this group[34][35].

The use of HFOs compounds has been studied by many researchers as an alternative to R134a refrigerant due to its thermodynamic properties. These studies compared the use of HFOs and R134a in relation to COP, energy consuming, the charge ratio, and others. Experimental study[36] for using R1234yf and R1234ze as alternative of R134a in two domestic refrigerators, One is a refrigerator with traditional technology, and the other is with advanced technology. In both refrigerators tested, R-1234yf and R-134a have similar energy consumption and capacities, indicating that R-1234yf might be used as a drop-in replacement for R-134a in residential refrigeration applications. In both Ref1 and Ref2, R-1234ze performed well in terms of energy usage. The decreased capacity of R-1234ze, on the other hand, resulted in longer compressor run times and fewer defrost cycles. Increasing the frequency of defrost cycles might reduce real-world energy efficiency. As a result, system adjustments would be required to account for R-1234ze's decreased capacity, rendering it unsuitable for use as a drop-in replacement for R-134a.

As the same, an energy analysis [37] in domestic refrigerator used R1234yf as drop-in replacement to R134a, showed when compared to R134a, the HFO refrigerant R1234yf has nearly identical volumetric cooling capacity, refrigerating impact, energy consumption, and coefficient of performance. As a result, it can be considered an appropriate alternative to HFC-134a.

Also, another theoretical study [38] confirmed the previous findings, it is shown that HFC-134a and HFO-1234ze have nearly identical COP and exergetic efficiency, with a difference of 5.6 percent, which reduces as evaporator temperature rises, but it is 14.5-5 percent greater than HFO-1234yf. As a result, at higher evaporator temperatures, HFO-1234yf can be a possible 'drop-in' replacement for HFC-134a, while HFO-1234ze can be a good replacement after some modifications. The COP and exergetic efficiency of HFC-134a are higher than those of HFO-1234yf, but they are lower than those of HFO-1234ze. When the effectiveness of the heat exchanger is increased from 0 to 1, however, the tendency reverses. Also another theoretical analysis showed that R1234ze(E) had a similar COP to R134a, but its cooling capacity was significantly lower[37].

An evaluation of energy performance[28] presented that the HFO refrigerant R1234yf reduces cooling capacity by 4.5 percent to 8.6 percent while increasing power consumption by 1.6 percent to 6.7 percent. As a result, the average COP is lowered by around 10%. As a result, it can be considered a direct drop-in replacement for R134a with a significant COP reduction, taking into account the A2L refrigerant's safety criteria. The hydrofluoroolefin R1234ze(E) results in a 24.9 percent and 17.8 percent reduction in cooling capacity and power consumption, respectively. This significant reduction emphasizes the requirement for a larger-displacement compressor to attain the same cooling capacity. As a result, the refrigerating plant's COP decreases by around 8.6%. It is not suitable for usage as a direct outcome, based on the findings.

4.2.2 Mixture of HFCs and HFOs as alternative of R134a

In a household refrigerator built to run with 100 g HFC134a, an experimental investigation compared the energy act of the blend of R1234ze(E)/R134a with mass ratio of (90/10), and the R1234ze(E). The cycle's draw down time was 4% faster with the binary mixture R134a/ R1234ze(E) than with R134a alone, and 9.6% faster than with pure HFO. When compared to R134a, after 24 hours of work, the energy savings was 14 percent and 5.6 percent for the blend and pure respectively [39].

As an alternative to R134a, a theoretical investigation [40] employed three blends, blend(1), blend(2) and blend(3). They were constitute of R152a and R1234ze(E), with mass ratios of 60:40, 50:50, and 40:60, respectively. Blend(2) was chosen as optimum R134a direct substitute. It also had GWP of 72, making it suitable for use in vapor compression systems, and volumetric cooling capacity similar to R134a. As a result, blend(2) can be utilized as a direct substitute for R134a without requiring any compressor modifications, especially COP increased 2% and 5% at condenser temperature of 45°C and 65°C respectively. The capacity of refrigeration for Blend(2) was found to be roughly 7% lesser comparing with R134a. The power consumed of blend(2) decreased by 10%, the temperature of compressor discharge was higher too, which could have a minor impact on compressor life. Because of the presence of R1234ze(E) in the combination, M2's flammability was lowered. If the original system compressor uses synthetic lubricant, M2 can be utilized as a drop-in replacement for R134a.

With the aim of replacing the refrigerant HFC-134a in a domestic refrigerator, an energy analytical study [37] employed R134a/R152a/R1234yf such as ARM42 (in the ratio of 8.5/14/77.5 by mass), ARM42a (in the ratio of 7/11/82 by mass). Theoretically, the study found that ARM42 and ARM42a consume less energy than HFC-134a at 300°C condenser temperatures. At 500C, however, the situation is completely flipped; the ARM42a consumes roughly 10% more power at this temperature. ARM42 has the lowest cooling capability of the three refrigerants, with ARM42a being nearly identical to R134a. In addition, when compared to R134a, these two refrigerants have lower pressure ratios. When compared to ARM42 and R134a, which both had identical volumetric cooling capacities, ARM42a had a greater volumetric cooling capacity. At a condenser temperature of 300°C, ARM42 and ARM42a had lower compressor discharge temperatures, but at 500°C, ARM42a had higher compressor discharge temperatures than ARM42 and R134a. So, based on an overall assessment of all refrigerant properties, we can conclude that ARM42a is a better direct substitute for HFC-134a in a household refrigerator when the appropriate safety conditions are met.

R134a/R1234yf (10:90, by weight) was used in an experimental study [41] to replace R134a in a refrigerator. The electrical energy consumption was reduced by 7.5 percent and the pull-down time was reduced by 14 percent in the binary mixture R134a/R1234yf. The amount of energy saved was reduced by 16%. The charge of refrigerant was 116 g, which was higher by 16 percent.

In the same way, as an alternative to R134a, another mixture used R134a/R1234yf (R513A) (44:56 by weight). The study [42] found that energy consumed was reduced by 3.5 percent and the capacity of refrigeration was increased, while the excellent mass of charge, which was being 80 gram, decreased to 5.9%.

R450A and R513A were studied to be R134a substitutions in another experiment[43]. The R450A had a lower mass flow rate of 9.2 percent, when the temperature of compressor discharge 93.1 ºC, and the volumetric capacity decreased by 7%, also the capacity of refrigeration reduced to 14.3 percent, and the COP decreased to 5.3, according to this study. R513A had a higher mass flow rate of 19.3 percent, a discharge temperature of 88.9 ºC, also the volumetric capacity of 1.5 percent, and cooling capacity of 2.5 percent, and a COP of 1.8 percent.

4.3 Hydrofluorocarbons (HFCs)

The most familiar form of organofluorine compounds are hydrofluorocarbons (HFCs), which are artificial organic molecules containing atoms of fluorine and hydrogen. At standard condition, these refrigerants are generally in the gaseous state. R134a is one of the greatest extensively used HFC refrigerants in air conditioning and as a refrigerant. HFCs were adopted to replace the more potent chlorofluorocarbons (CFCs) that were phased out by the Montreal Protocol and hydrochlorofluorocarbons (HCFCs) that are currently being phased out in order to promote the recovery of the stratospheric ozone layer. Older chlorofluorocarbons like R-12 and hydrochlorofluorocarbons like R-21 were superseded by HFCs[44][45][46].

Bolaji [47] performed an experimental study on the use of R32 and R152A as a substitute for R134a in a 120L household refrigerator, the researcher used the drop-in method, and found that biggest COP was achieved with R152a. The average COP achieved with R152a was 4.7% greater than R134a, but the average COP of R32 was 8.5% lesser than R134a. R152a provides the lowest power consumed. The compressor used 4.0% and 3.2% fewer energy when using R152a than using R134a and R32 in the system, respectively. The performance of R134a in the experimental refrigerator closely followed that of R152a. In general, the system performed better with R152a than with both R134a and R32. This shows that R152a can be used as an alternative refrigerant to R134a in a home refrigerator.

On the other hand, theoretical study [40] used R152a as alternative to R134a, the compressor discharge temperature, volumetric cooling capacity, cooling capacity, compressor power consumption, and coefficient of performance of the vapor compression system were all compared. When compared to R134a, the findings revealed that R152a had a higher coefficient of performance and nearly equivalent volumetric and cooling capacity; however, flammable R152a running at high compressor discharge temperatures was prohibited.

In addition, Gaurav and Kumar made an investigation in comparison of exergy and energy performance between R152a and R134a in domestic refrigerator [48]. The R152a achieved a higher COP and exergy efficiency compared to the R134a. In addition, power consumed decreased to 16 percent and the capacity of refrigeration decreased to 9.75 comparing with R134a.

Raskar and Mutalikdesai [49] also found that R152a had a 4.65 percent higher COP in the vapour compression system. While the results of [28] revealed that when using R152a, refrigeration capacity increased by 5.7 percent, while the power consumed decreased by 8.8 percent comparing with R134a system. COP was modestly enhanced from 1 percent to 4.8 percent. R152a's key advantages are its greater COP and low GWP, while the major disadvantages are the great temperature of discharge, furthermore it is a combustible refrigerant comparing with R134a. As conclusion, R152a could be a preferable option than R134a if protection actions are in place.

5. Result and discussion

Through this review, alternative refrigerants to R134a have been compared, and these alternatives have been categorized according to their types and mixtures of these refrigerants. The division of these refrigerants into pure HC and hydrocarbon mixtures with HFC, as well as pure HFO refrigerants, and their mixtures with HFC, and then HCFC refrigerants, and from natural refrigerants CO_2 is an example.

Studies were shown and compared by percentage of energy consumption as well as percentage of improvement in efficiency. The results of the studies showed that when using refrigerants R1234yf, R1234ze and R513A, there was a decrease in COP, while when using R450A the COP increased compared to R134a and through different operating conditions. R1234ze cannot be used as a substitute for R134a due to its low cooling capacity, while R1234yf can be used as a substitute due to its non-toxic and low flammability properties[50]. As for the mixtures, the studies showed that the mixture of R134a/R1234ze, 10/90% by weight, had lower energy consumption, while R1234ze and R513A had higher energy consumption. It is possible to use refrigerant R513a instead of R134a to reduce GWP because of its properties, it is non-toxic and non-flammable, and with regard to the refrigeration system, its discharge temperature is low.

Although both mixtures are within the safe categories (A1) according to ASHRAE classification and the GWP value of the R450A is 406, and for the R513a the GWP value is 573, which means that it is approximately half the GWP value of R134a; therefore, this shows that the use of these mixtures is a temporary solution because the plan is to reduce fluorinated gases, which have an impact on global warming.

Hydrocarbon refrigerants have many advantages that make them at the forefront of the alternatives to be used for R134a, and perhaps one of the most important advantages like good COP, compressor discharge temperature, and cooling capacity, in addition to being environmentally friendly. economically, because the density of hydrocarbon is less than that of R134a, so the quantity of the charge is less[51], this leads to a reduction in refrigerant emissions to the atmosphere.

Studies have shown that using R600a refrigerant as a substitute for R134a improved COP by 95%, while the drain temperature of the compressor decreased by 10%. Also, the amount of charge was reduced by 0.66 relative to R134a, while R290 achieved higher performance efficiency than R134a. However, the compressor power consumption increased by 44.8%, which necessitates an increase in the size of the compressor, so it is not recommended to be used as a drop-in substitute for R134a.

As for the hydrocarbon mixtures R600a/R290 50:50 by weight, studies showed that the charging mass was reduced by 50%, and the COP had improved by 3.6%, and the compressor temperature had decreased by 8.5-13.4 K, so it can be used as a drop substitute for R134a.

6. Conclusions

Through theoretical and practical studies, the following conclusions were obtained:

- R1234yf refrigerant is suitable as a substitute for R134a
- Refrigerant R1234ze is not suitable as a replacement due to its low cooling capacity, and this requires modifications to the mail system.
- R600a and R290a are not suitable as drop substitutes for R134a due to the high operating pressures, and this requires replacing the compressor.
- The R134a/R1234yf mixture is better than the alternative mixtures to R134a, it is less expensive and non-flammable.
- The R450a could be a replacement for the R134a with some modifications, but it has a high GWP so its use is limited.
- R513a can be a drop-in replacement for R134a, but its GWP is high and its use is limited.

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