Investigation of Environmentally-Friendly Alternative Refrigerants for Automotive Air Conditioning Systems

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Abstract. The popularity of automotive transport and the length of time people now spend in their cars mean that most vehicles come equipped with an automobile air conditioning (AAC) system. Most of these use refrigerant fluids, which affect the environment and increase global warming. Therefore, many territories have laws that mandate the use of environmentally-friendly refrigerants with zero ozone depletion potential (ODP) and low global warming potential (GWP). The ACCs in most existing motor vehicles use R134a as a refrigerant, which has a high GWP. The aim of this study is to investigate alternatives to R134a that are characterized by environmentally-friendly qualities such as low GWP, are available and can be charged directly into an existing system without modification. Therefore, thermodynamic analysis of an AAC system containing R134a was conducted and the results compared with blends formed by mixing hydrocarbons (HCs) (R290/R600a), which are flammable, environmentally-friendly and ultra-low GWP refrigerants, with R134a (R600a/R290/134a). The mixing of HC and R134a led to reduced flammability and used R134a in a ratio within low GWP criteria, to decrease the cost and the amount of its banked. Refprop software was used for the thermodynamic analysis. Theoretical results revealed that the blend of (R600a/R290/134a) with a mass ratio (43/35/22) has low GWP, provides the same level of refrigerant performance and can be used directly without any modification to the system.

Keywords: Automobile air conditioning system, R134a, alternative refrigerants, low GWP, HC
1. Introduction

Automobiles, particularly when driven during the day, generate a great deal of heat and increase the car’s temperature, making it uncomfortable, especially in hot weather. Therefore, automobile makers fit most models with an A/C system, generally with a chlorofluorocarbon (CFC) refrigerant [1].

In 1974 Molina and Rowland reported the hypothesis of ozone depletion, whereby the chlorine element catalytically demolished the ozone layer in the stratosphere. That layer has the important role of filtering harmful ultraviolet rays on their way to Earth [2]. A/C systems are acknowledged as the largest contributor of chlorine released into the atmosphere, due to regular and irregular leakage from the system.

In September 1987 an international convention called the Montreal Protocol, administered by the United Nations Environment Program, required the phasing out and ultimate termination of the use and production of CFCs [3]. The alternative product group was HFCs, like R134a, which have no impact on the ozone layer. However, HFC refrigerants do have a high GWP.

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### Nomenclatures

| Symbol   | Description                  | Unit   |
|----------|------------------------------|--------|
| \( h \)  | Enthalpy                     | kJ/kg  |
| \( P \)  | Pressure                      | bar    |
| \( P_{\text{cond}} \) | Condenser pressure           | bar    |
| \( P_{\text{evap}} \) | Evaporator pressure          | bar    |
| \( Pr \)  | pressure ratio               | ----   |
| \( q_{\text{evap}} \) | Refrigerating effect        | kJ/kg  |
| \( T, t \) | Temperature                 | °C     |
| \( w_{\text{comp}} \) | Specific work               | kJ/kg  |
| \( \rho \) | Density                     | kg/m³  |
| \( RE \)  | Refrigerating effect         | kJ/kg  |
| \( \text{VCC} \) | Volumetric Cooling Capacity | kJ/m³  |

### Abbreviations:

- AAC: Automobile Air Conditioning
- ASHRAE: American Society of Heating, Refrigerating and Air-Conditioning Engineers.
- CFC: Chlorofluorocarbon
- COP: Coefficient of performance
- GWP: Global warming potential
- HC: Hydrocarbon
- HCFC: Hydro-chlorofluorocarbon
- HFC: Hydro-fluorocarbons
- NIST: National Institute of Standards and Technology
- ODP: Ozone depletion potential
- P-h: Pressure–enthalpy diagram
- REFPROP: REFerence fluid PROPerties
- VCR: Vapour compression refrigeration cycle
- Mix: Mixture of refrigerants
Automobile air conditioning systems emit directly and indirectly, and are classified as major contributors to an increased greenhouse effect. These emissions constitute about 30% of worldwide hydrofluorocarbon emissions. So, it is desirable that a less harmful substitute is found for the refrigerant R134a, and this has been formalized in Europe according to directive 2006/40/EC. There, substitution began in January 2011 with newly-produced vehicles and was extended to all vehicles from January 2017. The alternative refrigerants must be environmentally friendly and have GWP below 150 [4]. Initially, automobile manufacturers improved R134a systems by reducing infiltration and research began, to find an alternative refrigerant to replace R134a.

Padalkar and Kadam (2010) [5] discussed the suitability of carbon dioxide (CO₂) in refrigeration and air conditioning systems: CO₂ is a natural gas, widely available, safe and environmentally-friendly refrigerant. It also has best thermophysical and transport properties, after ammonia. However, its low critical point is among the main disadvantages of CO₂. The lower critical temperature of CO₂ (31 °C), converts the subcritical vapor compression cycle into transcritical mode. The use of transcritical mode leads to reduced cooling capacity, high working pressure (reaching 3–4 times more than other refrigerants) and higher compressor power consumption which results in less energy efficiency of the system.

Esbría et al. (2013) [6] experimentally analyzed a vapor compression system using R1234yf as a drop-in replacement for R134a. The energy performance of both refrigerants was compared; comparisons took R134a as baseline. The results showed the cooling capacity of vapor compression system obtained with R1234yf is about 9% lower than that obtained with R134a in the studied range. In addition, the values for the COP system were about 19% lower with R1234yf than those obtained using R134a.

Gomaa (2015) [7] made a theoretical study of the possibility of using low-GWP refrigerants of R152a, R1234yf and R1234ze as substitutes for R134a in AAC, due to its high GWP. All refrigerants were investigated with different evaporating and condensing temperatures and refrigerant mass flow rates. The compressor power, cooling capacity, pressure ratio, condenser load and coefficient of performance (COP) for all refrigerants were compared. The results indicated that refrigerant R1234yf had the best thermal performance among all investigated refrigerants and was environmentally acceptable.

Vaghela (2017) [8] evaluated theoretically an R134a AAC system, using various refrigerants as a drop-in substitute. The thermodynamic properties of substituted refrigerants R290, R600a, R407C, R410A, R404A, R152a and R1234yf were compared to R134a and the thermodynamic analysis of all refrigerants were derived. The results showed R1234yf to have a lower COP compared to R134a, however R1234yf was the best suitable alternative refrigerants as a drop-in substitute with minimal modification.

Kandhaswamy et al. (2017) [9] experimentally evaluated the performance of an R134a AAC system by using a mixture of R134a and HC₃s as an alternative refrigerant. The mixture of R290/R600a (in the ratio of 50/50, by mass) was retrofitted to the system. The performances of R134a and its alternative were evaluated at different compressor speeds and with different load in cabin. The inlet air temperature to the condenser varied within the range 30–50 °C.

The results showed the alternative HC₃ mixture to have a faster cooling rate, due to its high latent heat of vaporization. Due to the higher refrigeration effect of HC₃s, the COP of the system was 5% higher than when using R134a. Due to HC₃s’ lower specific heat ratio, the compressor discharge temperature was 8–10 K lower, and compressor power consumption was 5% lower when using HC₃s, due to lower viscosity and lower liquid density. The charge size of R290/R600a mixture required by the system was about 50% less than for R134a.
The number of cars worldwide now exceeds 1.015 billion [10], and Iraq alone accounts for nearly 6 million of these [11]. Most motor vehicles use R134a as a refrigerant, but it has a high GWP. Therefore there is a need for alternative refrigerants which have a low GWP, are widely available, cheap, achieve the same or greater cooling capacity, show high COP in hot weather and can be added directly to an existing system without any modification.

Although CO₂ has good thermophysical and transport properties, its low critical point makes its working pressure very high [20], which in this context would necessitate the redesign of systems. Therefore, it was not included in this study.

In a similar way, R1243yf has a cooling capacity 9% lower than that obtained with R134a. The volumetric cooling capacity can be maintained within limits of (+8%) related to R134a, but this ratio demands a change in compressor size [17]. Also, it has low COP and costs nearly ten times more than R134a [12]. Thus, it is not suitable alternative refrigerant at this time.

A mixture of HCs (R290/R600) has good thermodynamic properties. It is available, cheap and has very low GWP. The key disadvantage it that it is highly flammable. The equivalent charge size of (R290/R600) mixture, for 1kg of R134a, is nearly 500g [13]. Therefore, a mixture of R134a and HCs within a ratio that ensures the mixture’s GWP remains within acceptable levels will reduce the flammability [3] and cost [12].

2. Thermodynamic Analyses

2.1 Thermodynamic analyses of refrigerant properties

The thermodynamic properties of R134a and HCs R290 and R600a were evaluated via the most widely-used refrigerant database software, known as REFPROP. This program was developed by the National Institute of Standards and Technology (NIST) in order to calculate the thermodynamics and the transport properties of industrially important fluids and their mixtures [14].

2.2 Thermodynamic analyses of refrigerant cycle

The results of thermodynamic properties of refrigerants carried out on standard rating vapor compression refrigeration (VCR) cycle are shown in Figure 1. It was assumed that in a steady state, 1 kg of refrigerant flows in the existing system, that the temperatures of the evaporator and condenser are 7.5°C and 55°C.

![Figure 1. Pressure-enthalpy chart of VCR [18]](image-url)
respectively [19], isentropic compressor efficiency unity, neglected the pressure drops in suction and discharge lines.

The system was analyzed in the following manner, with the help of steady flow energy equations. The refrigerating effect, which was the heat absorbed by the refrigerant in the evaporator \( q_{\text{evap}} \), kJ/kg was calculated as:

\[
q_{\text{evap}} = (h_1 - h_4),
\]  

\( h_1 \) = the refrigerant specific enthalpy at the outlet of the evaporator (kJ/kg); and \( h_4 \) = the refrigerant specific enthalpy at the inlet of the evaporator (kJ/kg). The work input to the compressor \( w_{\text{com}} \), kJ/kg was obtained as:

\[
w_{\text{com}} = (h_2 - h_1),
\]  

\( h_2 \) = refrigerant specific enthalpy at the outlet of the compressor (kJ/kg). The flow of refrigerant in the expansion valve from point 3 to point 4 has a constant enthalpy (isenthalpic). Therefore,

\[
h_3 = h_4,
\]  

\( h_3 \) = refrigerant specific enthalpy at the outlet of the condenser (kJ/kg). The pressure ratio (Pr) of the cycle was obtained as:

\[
Pr = \frac{P_{\text{cond}}}{P_{\text{evap}}}
\]  

Where \( P_{\text{cond}} \) = condensing pressure (bar) and \( P_{\text{evap}} \) = evaporation pressure (bar).

The volumetric cooling capacity (VCC, kJ/m^3) denotes as the volume of refrigerant handled by the compressor for the given fluid and calculated as follows:

\[
VCC = \rho_1 \times q_{\text{evap}},
\]  

Where \( \rho_1 \) = refrigerant density at the exit of the evaporator (kg/m^3).

The COP is the refrigerating effect produced per unit of required work; therefore, the COP was obtained as the ratio between Eq. (1) and Eq. (2):

\[
\text{COP} = \frac{q_{\text{evap}}}{w_{\text{com}}}
\]  

The GWP for R290, R600a and R134a are, 5, 20 and 1300 respectively [15]. The GWP of mixture can be calculated according to the equation below [16].

\[
\text{GWP of Blend} = (\% \text{ mass of component A} \times \text{GWP of A}) + (\% \text{ mass of component B} \times \text{GWP of B}) + (\% \text{ mass of component C} \times \text{GWP of C})
\]  

\( \text{GWP of Blend} \) = (\% \text{ mass of component A} \times \text{GWP of A}) + (\% \text{ mass of component B} \times \text{GWP of B}) + (\% \text{ mass of component C} \times \text{GWP of C})
3. Results and Discussion

The main parts of an AAC system are the heat exchanger (represented by an evaporator and condenser), compressor, expansion valve and connection tubes. The thermodynamic properties of any alternative refrigerant must work with existing parts of AAC systems that were originally intended for use with R134a.

The viscosity values of HCs at different saturation temperatures for vapor and liquid phase are shown in Figure 2. The values for the two phases were less than those for R134a, which mean the tubes and heat exchanger are suitable for use with them, and no further pressure drop would be obtained in the system.

Figure 3 illustrates the values of thermal conductivity for HCs, which were more than R134a for both phases, thus the design of existing heat exchangers intended for R134a is suitable for HCs and there would be no need to replace them.

Figure 4 shows that the lowest values for saturation vapor pressure are associated with R600a, while R290 has saturation vapor pressure values greater than those for R134a. Therefore, the choice of R290 alone as alternative would not be suitable for R134a AAC parts like heat exchangers, expansion valves and connection tubes. According to the saturation pressure values for R600a, the use of R600a alone would place the system under vacuum conditions and allow air to enter the system.

The compressor is an important part of any AAC system. It is expensive and difficult to change a compressor. To avoid that, the value of VCC for any alternative refrigerant must be near to that of R134a, in a range (+ 8%) [17]. The VCC value depends on the value of vapor density and the refrigerant’s latent heat. Figure 5 shows the HCs’ values of latent heat for various saturated temperatures, these values were 84% more than for R134a, but on the other hand, the density values for R290 and R600a were 31% and 70% less than for R134a, respectively, as can be seen in Figure 6. This means the VCC values for R290 will be more than R134a, and for R600 will be less, and this would require a change of compressor.

Our analysis of refrigerants’ properties explored the use of R290 and R600a alone as alternatives for R134a in current AAC systems. Mixing of R290 and R600a will normalize the pressure, but according the low VCC values of R600, the mass fraction of R290 must more than R600 to reach VCC values equivalent to R134a. In which case, the pressure would exceed the design value. Therefore, adding R134a to HCs with a mass fraction that would ensure the GWP of ternary mixture did not exceed allowable range, would normalize the pressure and VCC.

The charge size of refrigerant for most AACs with R134a, according the manuals, range from 1– 0.5 kg. The equivalent charge size of HCs mixed with R134a, according to the ratio of liquid density, is 0.5 [13]. According to the GWP value of R134a, the fraction of R134a must not exceed 22%. Therefore, the suggested mixtures were (R600a/R290/R134a) with the following mass ratios: Mix 1 (39/39/22), Mix 2 (43/35/22), Mix 3 (35/43/22) with equivalent charge size for 1kg of R134a nearly 500g.

Using the REFPROP program, the thermodynamic data for VCR at evaporator and condenser temperatures were 7.5°C and 55°C respectively, conducted for all of the alternative refrigerants mentioned. Figure 7 shows the high pressure (Ph), low pressure (Pl) and pressure ratio (Pr) for R134a, Mix 1, Mix 2 and Mix 3. The results showed the value of Ph for Mix 1 and Mix 2 to be nearly the same as R134a, but Mix 3 has a Ph greater than that of R134a by 4%, this returns to the high mass fraction of R290, so the increasing R290 mass fraction ratio will require modification of existing systems. The azeotropic behavior of the HC mixtures caused the evaporator output pressure for all mixtures greater than that of R134a. This led to reduced compression ratio and thus reduced the consumption power.
Figure 8 explains that the VCC value of Mix 1 is the same as that for R134a, but Mix 2 has 3% less and Mix 3 has 4% more than R134a. All mixtures showed acceptable VCC values. The COP values, which represent the ratio between refrigerant effect and compressor work for mixtures, showed small variation, about 1%, dependent on the ratio of R600a to R290. The GWP values for Mix 1, Mix 2 and Mix 3 are 147.87, 148.17 and 147.57 respectively, and all fall within low GWP range.

Figure 9 shows the alternative refrigerants that have been mentioned: R290/R600a with mass ratio 50/50 and R1234yf have VCC values of 11% less than R134a. Volumetric cooling capacity has a greater influence on the size of compressor as mentioned above, while mixed HCs with R134a obtained the same VCC values with acceptable pressures.
Figure 4. Pressure vs saturation temperature.

Figure 5. Latent heat vs saturation temperature.

Figure 6. Vapor density vs saturation temperature.
Figure 7. high pressure (Ph) vs Refrigerants, low pressure (Pl) and pressure ratio (Pr).

Figure 8. Volumetric cooling capacity and coefficient of performance as function of Refrigerants.
4. Conclusions

Many nations have legislated to ensure the use of environmentally-friendly refrigerants, and R134a has been phased out because it has high GWP. A comparison between the thermodynamic properties of R134a and the candidate refrigerants was achieved in this study. Theoretical analysis was carried out at 7.5°C evaporator temperature and 55°C condenser temperature, on standard VCR, for all alternative refrigerants that have been mentioned above. The following conclusions have been drawn.

1- Mixing R134a with R600a and R290 resulted in an 86.6% reduction in the GWP and remained within the constraint value level.

2- The use of R290 alone as alternative for R134a in AAC system would require modifications of the ACC system, because R290 has high pressure and VCC values.

3- The use of R600a alone as alternative for R134a in an AAC system would necessitate ACC system modifications because R600a has low pressure at design evaporator temperatures and may push the system into vacuum conditions. In addition, the VCC values for R600 are lower than for R134a, which would mean changing the compressor size.

Figure 9. Volumetric cooling capacity and coefficient of performance as function of Refrigerants.
4- The use of a mixture containing R290 and R600a as alternative for R134a in AAC systems with mass fractions that ensure acceptable work pressure will produce cooling capacity less than with R134a, which means the compressor size would have to be enlarged.

5- The addition of R134a with mass fraction 22% to HCs will increase the cooling capacity with acceptable work pressure.

6- Use the mixture of HCs and R134a reduced the charge size of HCs by 22% compared with use alone, which reduced the flammability.

7- The mixture R290/R600a with mass ratio 50/50 and R1234yf generated VCC values 11% lower than R134a, so would require a change of compressor to achieve the same performance.

8- The variation in COPs values was nearly 1%, Mix 2 having the same COP value as R134a.

9- All three mixtures (Mix 1, Mix 2 and Mix 3) can be used directly and without any modifications on existing 134a AAC systems but in light of the VCR results data, Mix 2 is preferred.

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