Thermodynamic study of environment-friendly R429A, R435A and R457A refrigerants as substitutes for ozone depleting R22 in refrigeration and air-conditioning systems

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ABSTRACT
Ozone depletion and global warming are presently the most serious global environmental problems and have led to drastic changes in the refrigeration technology. Therefore, environment-friendly refrigerants have attracted a significant attention. This paper presents the thermodynamic study of non-ozone depleting R429A, R435A and R457A refrigerants as substitutes for R22 in air-conditioning systems. The results obtained showed that the vapour pressure curves of R429A, R435A and R457A are very close to that of R22 with advantage of lower deviation in pressure. These refrigerants also exhibited lower pressure ratio and discharge pressure than R22 and their average discharge temperatures are 24.03, 13.54 and 28.53 % respectively lower than that of R22. They showed higher coefficient of performance than R22 with the average values of 2.47, 3.96 and 2.98 % respectively higher which shows better efficiency. The results also revealed R429A, R435A and R457A as energy efficient refrigerants as they exhibited lower power consumption per ton of refrigeration with average values of 2.14, 3.90 and 2.27 % respectively lower than that of R22. Generally, the three investigated environment-friendly refrigerants performed better than R22 and can effectively replace R22 in air-conditioning systems.

1 Introduction
Chlorofluorocarbons (CFCs) and Hydro-chlorofluoro-carbons (HCFCs) refrigerants used in refrigerating and air-conditioning systems have been known as one of the most harmful chemicals to the environment. These refrigerants have many suitable properties such as stability, non–toxicity, non–flammable, good material compatibility and good thermodynamic properties, which led to their common wide spread use and more preferable than the first generation refrigerants such as the toxic sulphur dioxide and ammonia, the less cyclically efficient carbon dioxide, and the flammable hydrocarbons used earlier in the century [1, 2].

The linkage of the CFC refrigerants to the damage of the ozone layer, which was established some decades ago, is attributable to their excellent stability because they can survive in the atmosphere for decades, eventually diffusing to the rarefied heights where the stratospheric ozone layer resides. The chlorine content of the refrigerants was the principal cause of destruction of the stratospheric ozone layer which absorbs the sun’s high energy ultraviolet rays and safeguards both humans and other living things from exposure to ultraviolet radiation. The hazard is represented by the refrigerant Ozone Depleting Potential (ODP) number [3-5].

The discovery of the depletion of the earth’s ozone layer has led to twenty-four nations and the European Community signing the Montreal Protocol in 1987, which regulates the production and trade of ozone depleting substances. Therefore, in January 1996, CFCs were banned in developed countries and their production and usage were prohibited completely all over the world in January 2010 [6, 7]. Moreover, the incompletely halogenated HCFCs (hydro-chlorofluorocarbons) such as R22, R123 and R124 will be phased out internationally by 2030 and 2040 in developed and developing countries respectively, because they still contain ozone depleting chlorine, though they are less destructive to the ozone layer and their ODPs are very small and less than those of CFCs [8, 9].
Over the decades, several chemicals have been proposed as alternative refrigerants; the selection of replacement substances has been motivated to avoid the shortcomings of the previous ones. With the phase-out of CFC and HCFC refrigerants under the Montreal Protocol, the refrigeration and air-conditioning industries have turned to hydro-fluorocarbons (HFCs) as substitutes. Therefore, atmospheric concentrations of CFCs are declining, while those of HCFCs and HFCs are rising rapidly [9, 10]. Recently, greenhouse warming has become one of the most significant global issues and the Kyoto protocol was proposed to resolve this issue, which classified hydro-fluorocarbons (HFCs) as part of the greenhouse warming gases [11-13].

HFC refrigerants are the prominent replacement for CFC and HCFC refrigerants, in refrigeration and air-conditioning systems. Although the ODP of HFC refrigerants is zero, and despite that they have lower Global Warming Potentials (GWPs) than many of the CFCs and HCFCs they are replacing, their GWPs are still very high. The heat trapping part of the HFCs are the Fluorine (F) atoms. The more fluorine and the more stable the molecule is, the higher the atmospheric lifetime and the GWP value turn out to be [14]. Consequently, application of HFC refrigerants as long-time substitute refrigerants in refrigeration and air-conditioning systems is not acceptable anymore and they need to be replaced by more environment-friendly refrigerants. The EU F-Gases Regulation and Mobile Air-Conditioning (MAC) directive have banned the use of R134a from 2011 in MACs of newly manufactured vehicles. The same MAC directive specifically prohibits the use of fluorinated greenhouse gases of which GWP is greater than 150 [15, 16].

R22 is the most commonly used refrigerant and propellant in various residential and commercial air-conditioning systems from small window units to large water chillers (medium temperature applications). Furthermore, among all refrigerants, R22 has the largest sales volume. It is a popular choice for equipment designers due to its high efficiency, capacity and low pressure. However, it belongs to the group of hydro-chlorofluorocarbon (HCFC) which contained the ozone depleting chlorine atom and is considered as a damaging working fluid to the environment. Many researches have been conducted within the last two decades to find suitable alternatives to R22. Motta and Domanski [17] carried out performance simulation of R22 and its alternative refrigerant (R410A) in an air-conditioner system with the outdoor air temperature ranged from 25.0°C to 55.0. The results obtained showed that the R410A system was normalized with respect to the performance of the R22 system over the entire temperature range, the R410A system’s energy efficiency ratio was approximately 2 % lower at 25.0°C and 6.5 % lower at 55.0°C.

Aprea and Greco [18] conducted performance analysis of R407C as R22 replacement in vapour compression refrigeration plant. The analysis was carried out with the help of exergetic approach. The exergetic performance of the individual components of the plant was analysed and showed that the performance of the R22 system is consistently better than that of the R407C system. Spatz and Motta [19] evaluated the performances of two HFC refrigerant mixtures (R407C and R410A) as substitutes for R22 in medium temperature refrigeration systems and the results showed that R410A is an efficient and acceptable option for R22 replacement in medium temperature applications.

Devotta et al. [20] carried out performance assessment of a window air-conditioner retrofitted with R407C as a substitute to R22. The results showed that the cooling capacity and coefficient of performance of the system working with R407C were lower in the ranges of 2.1 – 7.9 % and 7.9 – 13.5 % respectively than those of R22. The power consumption and the discharge pressure of the unit working with R407C were also higher in the ranges 6.0 – 7.0 % and 11.0 – 13.0 % respectively than those of R22 refrigerant. Chen [21] conducted a comparative study on the performance and environmental characteristics of R410A and R22 split-type residential air conditioner. The results showed that the use of R410A as a substitute to R22 improved the cooling capacity and the coefficient of performance of the system by 4% and 13.9% respectively.

Kalyani et al. [22] carried out an experimental analysis on a residential heat pump to study the performance of R22 and R407C. The results showed that at 35°C ambient temperature, R407C had 4.31% lower COP and 7.07% lower capacity compared to R22. Bolaji [23] investigated the performance of R22 and its two ozone-friendly alternative refrigerants (R404A and R507) in a window air-conditioner. Experimental results showed that R22 had the lowest pressure ratio and discharge pressure. The average discharge temperature obtained using R507 and R404A were 4.2% and 15.3% respectively higher than that of R22. The average refrigeration capacities of R507 and R404A were 4.7% higher and 8.4% lower respectively than that of R22.

Soni and Gupta [11] investigated theoretically the performance of vapour compression refrigeration cycle using R404A, R407C and R410A as alternatives for R22. The study showed that the COP and exergetic efficiency of R407C are better than those of R404A and R410A. Kundu et al. [24] presented an experimental study on heat transfer characteristics in evaporation of two R22 alternative refrigerants (zeotropic mixture R407C and quasi-zeotropic mixture R410A) through a small diameter (7.0 mm) smooth tube inclined at seven different angles from 0 to 90°. The investigation showed that the heat transfer characteristic of R410A was better than that of R407C at all inclinations of the tube. Sachdeva and Jain [25] carried out a comparative exergetic analysis of vapour compression refrigeration system using R134a, R407C and R410A as alternatives to R22 refrigerant. The results showed that the exergetic efficiency of R22 was higher than those of the three alternative refrigerants. The performance of R407C was very close to that of R22.

Various studies reviewed above presented R407C, R410A, R404A and R507A as prominent substitute refrigerants.
Refrigerants for R22. However, these are refrigerant mixtures that consist of HFC refrigerants and their GWP as shown in Table 1 are relatively high which made them not to be environmentally acceptable [26] or not suitable for long-term solutions to R22. Therefore, in this study, the performances of three non-ozone depleting and very low global warming potentials refrigerants (R429A, R435A and R457A) were investigated theoretically and compared with that of baseline refrigerant (R22). The thermo-physical and environmental properties of investigated refrigerants are shown in Table 2.

Table 1 Environmental Effect of Some HFC Refrigerant Mixtures and Investigated Refrigerants [27, 28].

| Refrigerants | Ozone depleting potential (ODP) | Global warming potential (GWP) (100 years’ horizon) |
|--------------|---------------------------------|--------------------------------------------------|
| R22          | 0.055                           | 1810                                             |
| R404A        | 0                               | 3922                                             |
| R407C        | 0                               | 1774                                             |
| R410A        | 0                               | 2088                                             |
| R417A        | 0                               | 2346                                             |
| R507A        | 0                               | 3985                                             |
| R508A        | 0                               | 13210                                            |
| R429A        | 0                               | 14                                               |
| R435A        | 0                               | 27                                               |
| R457A        | 0                               | 139                                              |

Table 2 Thermo-physical and Environmental Properties of Investigated Refrigerants [27, 29].

| Properties                              | Refrigerants |
|-----------------------------------------|--------------|
|                                         | R429A        | R435A        | R457A        | R22          |
| Molar mass (kg/kmol)                    | 50.76        | 49.04        | 90.85        | 86.47        |
| Critical Temperature (°C)               | 121.95       | 123.06       | 98.65        | 96.15        |
| Critical Pressure (MPa)                 | 4.73         | 5.19         | 3.95         | 4.99         |
| Liquid Density, kg/m³ at 25°C           | 642.21       | 694.98       | 1033.90      | 1190.70      |
| Vapour Density, kg/m³ at 25°C           | 13.50        | 13.88        | 31.21        | 44.23        |
| ODP                                     | 0            | 0            | 0            | 0            |
| GWP                                     | 14           | 27           | 139          | 1810         |
| GWP percentage of baseline refrigerant (%) | 0.77        | 1.49         | 7.68         | 100          |

2 Materials and methods

2.1 Analysis of refrigeration cycle

The majority of modern refrigeration and air-conditioning systems operate based on the principles of vapour compression refrigeration system. This system uses various refrigerants as working fluids depending on the type of application. The refrigerant circulates in the cycle to absorb and remove heat from the refrigerating chamber (evaporator) and subsequently rejects that heat at the condenser. The schematic diagram of a vapour compression refrigeration system is shown in Figure 1. It simply consists of four major components: two heat exchangers (an evaporator and a condenser), an expansion valve and a compressor. The four components constitute the following four processes that formed a complete cycle: isobaric heat rejection and condensation in the condenser, a constant enthalpy expansion process in the expansion device, isobaric heat absorption and evaporation in the evaporator and an isentropic compression process in the compressor. Pressure drops in the condenser and evaporator coils are assumed to be negligible so that the evaporation and condensation processes can be treated as constant-pressure processes. The heat transferred to the refrigerant in the evaporator is referred to as refrigerating effect. For the purpose of rating the system’s performance either for heating or cooling application, the efficiency term is the coefficient of performance (COP). It is the ratio of desired output (the refrigerating effect) to the work input which, in this case, is the work input to the compressor.

Figure 1 Schematic Diagram of a Simple Vapour Compression Refrigeration System

Figure 2 Vapour Compression Refrigeration Cycle on P-H Diagram
Considering the ideal refrigeration system on the p-h diagram showed in Figure 2, the followings are the summary of work or heat transfer in each of the processes [30]:

(a) Compression process: isentropic compression in the compressor from point 1 to point 2 and the work input \( W_{\text{comp}} \) (kJ/kg) is computed as:

\[
W_{\text{comp}} = (h_2 - h_1)
\]  
(1)

where, \( h_1 \) = specific enthalpy of the vapour refrigerant at the inlet of the compressor (kJ/kg); and \( h_2 \) = specific enthalpy of the vapour refrigerant at the outlet of the compressor (kJ/kg).

(b) Condensation process: de-superheating at constant pressure \( (P_c) \) from compressor discharge temperature \( (T_c) \) at point 2 to condenser temperature \( (T_{\text{c}}) \) at point 2', followed by a condensation at both constant temperature \( (T_{\text{c}}) \) and constant pressure \( (P_{\text{c}}) \) from point 2' to point 3. The heat rejected in the condenser is calculated as:

\[
Q_{\text{cond}} = (h_2 - h_3)
\]  
(2)

where, \( Q_{\text{cond}} \) = heat rejected in the condenser (kJ/kg); \( h_2 \) = specific enthalpy of the liquid refrigerant at the outlet of the condenser (kJ/kg).

(c) Expansion process: expansion at constant enthalpy in the throttling valve (capillary tube) from point 3 to point 4. Therefore,

\[
h_3 = h_4
\]  
(3)

where, \( h_3 \) = specific enthalpy of refrigerant at the inlet of the evaporator (kJ/kg).

(d) Evaporation process: evaporation at constant pressure \( (P_r) \) and constant temperature \( (T_r) \) in the evaporator from point 4 back to point 1. The heat absorbed by the refrigerant in the evaporator is given as:

\[
Q_{\text{evap}} = (h_1 - h_4)
\]  
(4)

where, \( Q_{\text{evap}} \) = refrigerating effect (kJ/kg).

For refrigeration application, the coefficient of performance \( (\text{COP}) \) is the refrigerating effect produced per unit of work required; therefore, \( \text{COP}_{\text{ref}} \) is obtained as the ratio of Eq. (4) to Eq. (1). This is expressed as:

\[
\text{COP}_{\text{ref}} = \frac{Q_{\text{evap}}}{W_{\text{comp}}}
\]  
(5)

The pressure ratio \( (P_{r}) \) of the cycle is obtained as:

\[
P_{r} = \frac{P_{\text{cond}}}{P_{\text{evap}}}
\]  
(6)

where, \( P_{\text{cond}} \) = absolute condensing pressure (MPa) and \( P_{\text{evap}} \) = absolute evaporating pressure. The specific power consumption is a useful indicator of the energy performance of the refrigeration system. This is obtained as power per ton of refrigeration \( (\text{PPTR}) \) and is expressed as [31]:

\[
\text{PPTR} = \frac{3.5W_{\text{comp}}}{Q_{\text{evap}}}
\]  
(7)

2.2 Thermodynamic properties of refrigerants

Refrigerant’s properties are necessary to describe the operating characteristics of the refrigerant within a system. The applicability of a refrigerant under design operating conditions is determined by its physical properties, while the thermodynamic and transport properties of a refrigerant are the useful and necessary parameters required to predict the system behaviour and the performances of the components. The thermo-physical properties of the investigated refrigerants were obtained using REFPROP software [29]. REFPROP is the most widely used refrigerants database. It was developed and is maintained by the National Institute of Standards and Technology (NIST). The software is based on the most accurate pure fluid and mixture models. It employs three models for the thermodynamic properties of pure fluids: equations of state explicit in Helmholtz energy, the modified Benedict-Webb-Rubin equation of state, and an Extended Corresponding States (ECS) model. Mixture calculations employ a model that applies mixing rules to the Helmholtz energy of the mixture components; it uses a departure function to account for the departure from ideal mixing [29]. The cycle data are calculated based on the fluid properties and they were used to predict the basic performances of the new alternative refrigerants (R429A, R435A and R457A) and compare them to the baseline refrigerant (R22).

3 Results and Discussion

The variation of the vapour pressure with saturation temperature for R22 and its three investigated alternative refrigerants (R429A, R435A and R457A) are shown in Figure 3. It is clearly shown in this figure that the vapour pressure curves for the alternative refrigerants are very close to the curve of R22 (the baseline refrigerant) with advantage of slightly lower deviation in pressure. This shows that these refrigerants can exhibit similar properties.

Figure 4 shows the variation of the compressor pressure ratio with the evaporating temperature for the four investigated refrigerants. The pressure ratio reduces as the evaporating temperature increases for all the refrigerants. Compressor pressure ratio is one of the conditions use for choosing suitable alternative to any refrigerant in refrigeration and air-conditioning systems. Alternative refrigerants with pressure ratios similar to or lower than that of the existing refrigerant they want to replace are more suitable than those with higher pressure ratios, because high pressure ratio will be detrimental to the system's performance. As shown in Figure 4, the pressure ratios for R429A, R435A and R457A are very close, but slightly lower than that of the baseline refrigerant (R22).
Their average values between the temperature range from -30 to 10 °C are 6.92, 2.73 and 5.07 % respectively lower than that of R22.

Very high latent heat energy is desirable since the mass flow rate per unit of capacity is less. When the latent value is increased, the energy efficiency and capacity of the compressor are significantly increased. The curve of the refrigerating effect obtained using R457A is similar to that of R22, while R429A and R435A exhibited much higher refrigerating effect than R22 as clearly shown in Figure 5. The average refrigerating effects of R429A and R435A refrigerants between the temperature range of -30 to 10 °C are 129.39 and 152.24 kJ/kg respectively higher than that of R22.

The influence of evaporating temperature on the refrigerating effect for R22 and its investigated alternative refrigerants is shown in Figure 5. As shown in the figure, the refrigerating effect increases as the evaporating temperature increases for all the investigated refrigerants. The latent heat of refrigerant increases as its evaporating temperature increases which also increases the heat ab-
The variation of the discharge temperature for R22 and its three investigated alternative refrigerants (R429A, R435A and R457A) as a function of the evaporating temperature is shown in Figure 6. High discharge temperature is harmful to the performance of the system. The use of refrigerants with low discharge temperature as drop-in substitutes for refrigerant in an existing system will produce less strain on the compressor and therefore increase the compressor’s life. As shown in Figure 6, the discharge temperature reduces as evaporating temperature increases. All the three alternative refrigerants exhibited lower values of the discharge temperature than R22. The average discharge temperatures obtained for R429A, R435A and R457A were 24.03, 13.54 and 28.53 % respectively lower than that of the baseline refrigerant (R22).

The discharge pressures at condensing temperature of 40°C for R22 and its three investigated refrigerants (R429A, R435A and R457A) are shown in Figure 7. The discharge pressure is a vital factor that affects the performance of a refrigerating system. It affects the stability of the lubricant and compressor components. Therefore, alternative refrigerants with discharge pressures similar to or lower than that of the existing refrigerant they want to replace will be more beneficial to the system’s performance. All the three alternative refrigerants exhibited low discharge pressure and the lowest value was obtained using R429A in the system.

The influence of the evaporating temperature on the coefficient of performance (COP) for the four investigated refrigerants is shown in Figure 8. The COP of a refrigeration cycle reflects the cycle performance. As shown in the figure, the COP increases with increase in the evaporating temperature for all the investigated refrigerants. The three alternative refrigerants exhibited very close and similar COPs to that of baseline refrigerants (R22). The average COPs obtained for R429A, R435A and R457A were 2.47, 3.96 and 2.98 % respectively higher than that of R22.

The curves of the power per ton of refrigeration (PPTR) at varying evaporating temperature for R22 and its three investigated alternative refrigerants are shown in Figure 9. The figure revealed that the power consumption per ton of refrigeration reduces as the evaporating temperature increases for all the investigated refrigerants. The curves for the alternative refrigerants are almost the same with that of baseline refrigerant, which shows similar performance in the system. The results also revealed the three alternative refrigerants as energy efficient refrigerants as they exhibited slightly lower power consumption than R22. The average PPTR obtained for R429A, R435A and R457A were 2.14, 3.90 and 2.27 % respectively lower than that of R22.
4 Conclusion

Based on the investigation results, the following conclusions are drawn:

(i) The vapour pressure curves of the three investigated alternative refrigerants (R429A, R435A and R457A) are very close to that of R22 (the baseline refrigerant) with advantage of slightly lower deviation in pressure.

(ii) R429A, R435A and R457A exhibited low pressure ratio with average values of 6.92, 2.73 and 5.07 % respectively lower than that of R22 between the temperature range of -30 to 10 °C.

(iii) The refrigerating effect of R457A is similar and almost the same with that of R22, while R429A and R435A exhibited much higher refrigerating effect with average values of 129.39 and 152.24 kl/kg respectively higher than that of R22 between the temperature range of -30 to 10 °C.

(iv) R429A, R435A and R457A showed advantages of low discharge pressures and temperatures over R22 refrigerant. The average discharge temperatures obtained for R429A, R435A and R457A were 24.03, 13.54 and 28.53 °C respectively lower than that of R22.

(v) The three alternative refrigerants exhibited slightly higher coefficient of performance (COP) than R22, which shows better efficiency and low operating cost. The average COPs obtained for R429A, R435A and R457A were 2.47, 3.96 and 2.98 % respectively higher than that of R22.

The results also revealed R429A, R435A and R457A as energy efficient refrigerants as they exhibited slightly lower power consumption per ton of refrigeration with average values of 2.14, 3.90 and 2.27 % respectively lower than that of R22.

Generally, all the three investigated alternative refrigerants performed better than R22; their specific power consumptions were less than that of R22, they also exhibited lower discharge temperature, discharge pressure, pressure ratio and higher COP than R22.

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