Performance Study of Vapor Compression Refrigeration System using Different Refrigerant Mixtures: Numerical Analysis

Rifat Bin Zakir*, Mohammad Arif Hasan Mamun
Department of Mechanical Engineering, Bangladesh University of Engineering and Technology, Dhaka-1000, BANGLADESH

ABSTRACT
Binary refrigerant mixture, a mixture of two refrigerants, is used rather than a single refrigerant in a refrigeration system to increase the performance and energy efficiency. In the present study, in pursuit of finding a better alternative refrigerant, numerical analysis of five types of mixtures, namely R600a-R134a, R152a-R600a, R290-R600a, R600a-R717 and R134a-R152a in a vapor compression refrigeration system (VCRS) has been done. The selection was based on the potential risk to the environment caused by the binary mixture. Ozone Depletion Potential (ODP) and Global Warming Potential (GWP) were the key factors of consideration in terms of environmental risk. The analysis tool used for the computations in the VCRS was Aspen HYSYS. For each case, a particular composition of a single refrigerant mixture was considered in this refrigeration system. The refrigeration effect (RE), compressor work (Wc), coefficient of performance (COP), dew point (T\text{dew}) and temperature glide (AT\text{glide}) were calculated with respect to the molar fraction and mass fraction of a single refrigerant. The calculations were performed with the help of few predefined parameters: composition of the mixture, condenser temperature, mass flow rate of the refrigerant mixture, pressure rise in compressor and pressure drop in expansion valve. Based on the results of the investigation, it can be declared that among these five mixtures, R600a-R134a mixture gave the best COP. But maximum COP was obtained for pure R600a. On the basis of temperature glide, it was found that except for the R152a-R134a mixture, all of the remaining four mixtures behaved as zeotropic mixtures.

Keywords: Binary refrigerant mixture, vapor compression refrigeration system, COP, temperature glide.

1. Introduction
A refrigerant is used as a working fluid in a refrigeration system to absorb heat from lower temperature and release that heat to a higher temperature. Many studies have been concentrated on the research of refrigerant mixtures. Didion et al. [1] indicated that with the long-term concerns about global warming and energy efficiency, the use of zeotropes will probably have a great influence on the refrigeration industry. Abu-Eishah [2] calculated the vapor—liquid equilibrium data for several binary CFC and non-CFC mixtures. Richardson et al. [3] showed that R290 and R290-R600a mixtures give better COPs than R12 under the same operating conditions in an unmodified R12 system. Experimental results of Jung et al. [4] indicated that R290-R600a mixture with 60% mass fraction of R290 has higher COP than R12. Chen et al. [5] presented a modified vapor compression refrigeration cycle (VCRC) using R290-R600 for freezers. Shaik et al. [6] investigated theoretical thermodynamic performance of a 0.8 TR window AC with ten binary refrigerant mixtures consisting of R1270 and R290 based on actual VCRC. Yan et al. [7] proposed a modified refrigeration cycle using refrigerant mixture R170-R290 for applications in low-temperature freezers.

Now, to calculate the performance parameters of the binary mixtures in the VCRS, a two-parameter Equation of State (EOS) can be used. In this research work, the main objective was to find a better alternative refrigerant in place of R600a in a VCRS. In pursuit of this, we have considered using binary refrigerant mixtures instead of a single refrigerant in the VCRS - the aim was to solve the Peng-Robinson equation of state [8] using Aspen HYSYS software to determine RE, Wc, COP, T\text{dew}, T\text{bubble} and AT\text{glide} of the 5 types of mixtures based on the molar fraction and mass fraction of constituent refrigerants.

However, in the 21st century, the two terms that are most acquainted with are global warming and ozone depletion. While choosing binary mixtures as refrigerant, ODP and GWP of the constituent refrigerants were considered. ODP and GWP for an individual refrigerant were given by Klein et al. in [9], and are provided in Table 1. As we can see, the refrigerants we have chosen, all have 0 ODP. So, their ODP will be 0 in the mixture as well. But as we are using these refrigerants as a binary mixture in the VCRS, their GWP will not be the same as their individual ones. The GWP of a mixture is calculated as a weighted average, derived from the sum of the mass fractions of the individual substances multiplied by their GWP. According to this equation, regardless of molar or mass fraction of any mixture, the maximum GWP will be found for pure R134a (GWP 1300) and minimum GWP will be for pure R717 (GWP 0). It means that for any mass or molar fraction of these 5 types of binary mixtures, the GWP will be between 0 and 1300. Now,
• If GWP<150, then the GWP of the refrigerant is categorized as low.
• If 150≤GWP≤2500, then the GWP of the refrigerant is categorized as medium.
• If GWP>2500, then the GWP of the refrigerants is categorized as high.
So, for any composition of the binary refrigerant mixtures considered in this research work, will have either low GWP or medium GWP. So, these binary refrigerant mixtures will be environment friendly.

* Corresponding author. Tel.: +88-01746763888
E-mail addresses: rifat135.me@gmail.com
2. Governing equation

The Peng-Robinson equation of state for a mixture is presented as:

\[ P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \]  

This equation can be rewritten in a cubic form as:

\[ Z^3 - (1-B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \]  

Here, \( Z = \frac{P_v}{RT}, A = \frac{aP}{RT^2}, B = \frac{bP}{RT} \).

Now, for Enthalpy calculation, the molar specific enthalpy of mixing can be calculated as:

\[ \Delta \tilde{h}_{mix} = \sum_{i=1}^{m} X_i \tilde{h}_{dep,i} - \tilde{h}_{dep} \]  

Here, \( \tilde{h}_{dep,i} \) is the molar specific enthalpy departure for pure gas \( i \) and \( \tilde{h}_{dep} \) is the molar specific enthalpy departure for the mixture calculated using the Peng-Robinson Equation of state as:

\[ \tilde{h}_{dep,i} = RT(1-Z_i) + \left( \frac{a_i - T \frac{da_i}{dT}}{2 \sqrt{2b_i}} \right) \ln \left( \frac{Z_i + 2.414B_i}{Z_i - 0.414B_i} \right) \]  

\[ \tilde{h}_{dep} = RT(1-Z) + \left( \frac{a - T \frac{da}{dT}}{2 \sqrt{2b}} \right) \ln \left( \frac{Z + 2.414B}{Z - 0.414B} \right) \]  

3. Numerical Modeling

In this study, five types of binary refrigerant mixtures were considered, namely, (1) R600a-R134a, (2) R600a-R152a, (3) R600a-R290, (4) R600a-R717, (5) R152a-R134a. Each of these mixtures can be varied in their composition based on the molar fraction as well as mass fraction of the constituents. For example, to determine the thermodynamic properties of a VCRS using A-B mixture, the composition has to be kept fixed. If we consider a composition system based on molar fraction, then \( X_A + X_B = 1 \). Here, \( X_A = \) molar fraction of A and \( X_B = \) molar fraction of B. Same rule applies for mass fraction, i.e., sum of mass fractions, \( W_A + W_B = 1 \).

For the present study, 11 types of composition for each of molar and mass fraction (\( X_A = 0 \) through to \( X_A = 1 \), and \( W_A = 0 \) through to \( W_A = 1 \)) were considered for A-B mixture. So, for 5 types of binary mixtures, a total of 55 cases of composition were considered for each of molar and mass fraction. Each of these compositions was used individually in the VCRS. Then \( RE, W_{in}, \text{ COP}, T_{evap}, T_{dew}, \) and \( \Delta T_{gibbs} \) were calculated for each composition. The following predefined parameters were assumed for simulations of every composition:

- The composition of the mixture
- Mass flow rate = 6.12 kg/h
- Condenser Temperature = 35°C
- Higher Pressure = 1500 kPa
- Lower Pressure = 101 kPa

With these predefined parameters, the governing equations were applied to the compressor, condenser, expansion valve and evaporator of the VCRS model, as given in Fig.1, and were simulated in Aspen HYSYS.

4. Results and discussion

The numerical procedure involving the solution of the Peng-Robinson equation of state using Aspen HYSYS adapted in the current study was validated against experimental data presented by Mohanraj et al. [10], where \( W_{R290} = 0.452 \) and \( W_{R600a} = 0.548 \) were used as mixture composition to determine the saturation pressures of the mixture for saturation temperatures ranging from -30°C to 60°C. As can be seen on Fig.2, the numerical data from Aspen HYSYS is in good agreement with the experimental work of Mohanraj et al.

![Fig.1 VCRS model in the software.](image)

![Fig.2 Validation of numerical method.](image)
For Fig.3-6 (a)-(d), molar fraction of R600a is shown, meaning that the other constituent refrigerants are R134a, R152a, R290, R717 respectively. For Fig.3-6 (e), molar fraction of R152a is shown, which means the other constituent refrigerant is R134a.

From Fig.3 (a) and (b), all RE and W\textsubscript{in} curves show a similar trend. Both the RE and W\textsubscript{in} curves increase with the increment of X\textsubscript{R600a} in the respective mixtures. It is because, at both higher and lower pressures, h\textsubscript{dep,R600a} is more than h\textsubscript{dep,R134a} and h\textsubscript{dep,R152a}. Fig.3 (e) also shows a similar variation, because at all pressures, h\textsubscript{dep,R152a} is more than h\textsubscript{dep,R134a}. So, when the amount of refrigerant with higher h\textsubscript{dep} is increased in the mixture, the resultant \(\Delta h\textsubscript{mix} \) value rises, which eventually causes increase of both RE and W\textsubscript{in}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig3a.png}
\caption{RE, W\textsubscript{in} and COP at various concentrations (molar fractions) of the mixtures.}
\end{figure}

For Fig.3 (c), the h\textsubscript{dep,R600a} is higher than h\textsubscript{dep,R290} at lower pressure. As evaporator works at lower pressure (101 kPa), RE increases with the increment of X\textsubscript{R600a} in the mixture. But at higher pressure (1500 kPa), h\textsubscript{dep,R290} is higher. That is why and since compressor works at higher pressure, W\textsubscript{in} decreases with the increment of X\textsubscript{R600a} in the mixture. For this reason, R600a-R290 mixture is more suitable compared to R600a-134a and R600a-R152a. Now for Fig.3 (d), both RE and W\textsubscript{in} decrease with the increase of X\textsubscript{R600a}. It is due to the stark contrast between the properties (\(\omega, \bar{v}_{cr}, P_{cr}\)) of R600a and R717. This sort of difference occurs because R600a is a HC and R717 is a non-HC. The COP curves for Fig.3 (a)-(c) depend on the trend of RE and W\textsubscript{in} as it is the ratio of RE to W\textsubscript{in}.

For Fig.4 (a)-(e), all the RE and W\textsubscript{in} curves show a similar trend with the RE and W\textsubscript{in} curves of Fig.3 (a)-(e).
and mass fraction do not represent the same concept. Had the binary mixture been formed with constituent refrigerants of equal molecular mass, then $RE$, $W_m$ and $COP$ curves of both molar and mass fraction would have been the same. Since the molecular mass of constituent refrigerants varies significantly in R600a-R134a, R600a-R717 and R152a-R134a, $COP$ curves of Fig.4 (a), (d) and (e) vary considerably with Fig.3 (a), (d) and (e) respectively.

Discussions regarding Fig.3 and Fig.4 lead us to the conclusion that, for A-B refrigerant mixture, where A, B both are HCAs and A has higher $h_{dop}$ than B, the highest $COP$ will be achieved for the composition with $X_A = 1$ or $W_A = 1$, meaning that the mixture needs to consist of A only. On the other hand, for that mixture, the lowest $COP$ will be achieved for the composition with $X_A = 0$ or $W_A = 0$, indicating that the mixture has to consist of B only. $COP$ values for the rest of the compositions will be anywhere between these two values, increasing with the increment of A in the mixture. When one of the constituent refrigerants of the mixture is non-HC, this trend in the $COP$ values was not observed. Another noteworthy finding from Fig.3 and Fig.4 was that, although R600a-R290 mixture provided the best $COP$ curve among these 5 mixtures, the maximum $COP$ was obtained for pure R600a, which indicated that, for the particular predefined parameters selected in this study, no composition of these 5 mixtures is a better alternative to R600a in terms of $COP$.

Now, from Fig.5 (a), (b) and (c), three mixtures: R600a-R134a, R600a-R152a and R600a-R290 show a similar trend of curves for $T_{dew}$, $T_{bubble}$ and $\Delta T_{glide}$. The reason behind this similarity is that these three mixtures are HC-HC mixtures. For all of these mixtures, the maximum $\Delta T_{glide}$ is found when the combination used in the VCRS is $X_{R600a} = 0.5$. Due to this high value of $\Delta T_{glide}$, these three mixtures should be included as azeotropically mixed. The only difference among these three mixtures is that, $T_{dew}$, $T_{bubble}$ and $\Delta T_{glide}$ do not possess similar range. In Fig.5 (d), for R600a-R717, an irregularity is noticed in the curves until $X_{R600a} = 0.2$. For the combinations where $X_{R600a} > 0.2$, the curves show similar trend like Fig.5 (a), (b) and (c). It is because R600a-R717 is a HC-nonHC mixture.

*Fig.4 RE, $W_m$ and COP at various concentrations (mass fractions) of the mixtures.*

It is noteworthy that $RE$ and $W_m$ for a particular composition (i.e. $W_{R152a} = 0.5$, $W_{R134a} = 0.5$) are not the same for a composition with similar molar fraction ($X_{R152a} = 0.5$, $X_{R134a} = 0.5$). It is because molar fraction...
Fig. 5 $T_{dew}$, $T_{bubble}$ and $\Delta T_{glide}$ at various concentrations (molar fractions) of the mixtures.

The dissimilarity in their properties cause this sort of irregularity in their performance parameters. However, as the maximum $\Delta T_{glide}$ for this mixture is much greater than 0°C, it can be concluded that this mixture is a azeotropic mixture. For R152a-R134a, Fig.5 (e), there is a very little gap between $T_{dew}$ and $T_{bubble}$ curve, which explains the lower values of $\Delta T_{glide}$ curve. This gradually increasing and then decreasing trend is similar to Fig.5 (a), (b) and (c) and it is because R152a-R134a is a HC-HC mixture as well. The maximum $\Delta T_{glide}$ value, which is very close to 0, verily concludes that this is a near-azeotropic mixture, if not an azeotropic one.

Now, as the molecular mass of constituent refrigerants varies significantly in R600a-R134a, R600a-R717 and R152a-R134a, Fig.6 (a), (d) and (e) show considerable difference in $T_{dew}$, $T_{bubble}$ and $\Delta T_{glide}$ curves with Fig.5 (a), (d) and (e). But the molecular masses of R600a, R152a and R290 are close to each other, which explains why Fig.6 (b) and (c) look considerably similar to Fig.5 (b) and (c). Fig.6 (a)-(d) give $\Delta T_{glide}$ with values greater than 0, which indicates that the four mixtures in these figures are zetotropic in nature. Fig.6 (e) shows $\Delta T_{glide}$ with values very close to 0, which confirms that R152a-R134a mixture is a near-azeotropic one. The significant irregularity of curves in Fig.6 (d), is due to the variation of constituent properties as R600a is a HC and R717 is a non-HC and due to the large difference between the molecular mass of the constituent refrigerants. If we pick any one of the combinations from Fig.6 (d), convert the mass fraction to the equivalent molar fraction and look for relevant data (i.e. $T_{dew}$, $T_{bubble}$ and $\Delta T_{glide}$) for that molar fraction from Fig.5 (d), these two data will be identical.
The following conclusions can be drawn from the numerical solutions of the Peng-Robinson equation of state using Aspen HYSYS software. 

- Pure R600a provides the best COP.
- R600a-R290 mixture gives the best performance among these 5 mixtures.
- R152a-R134a mixture is a near-azeotropic mixture. The other mixtures are zebotropic mixtures.
- It is better to use HC-HC mixture rather than using a HC-nonHC mixture to avoid irregularity.

6. References


NOMENCLATURE

\( Z \) : compressibility factor \\
\( T \) : temperature, °C \\
\( P \) : pressure, kPa \\
\( \bar{\rho} \) : molar specific volume, m\(^3\)kg\(^{-1}\)mol\(^{-1}\) \\
\( R \) : molar gas constant, J K\(^{-1}\)mol\(^{-1}\) \\
\( a \) : equation of state attraction parameter \\
\( b \) : Van der Waals covolume \\
\( \bar{h}_{dep} \) : molar specific enthalpy departure, kJ kg\(^{-1}\)mol\(^{-1}\) \\
\( \Delta h_{mix} \) : molar specific enthalpy of mixing, kJ kg\(^{-1}\)mol\(^{-1}\) \\
\( X_i \) : molar fraction of \( i \)th refrigerant component \\
\( \omega \) : acentric factor \\
\( P_{cr} \) : critical pressure, kPa \\
\( \bar{v}_{cr} \) : molar sp. volume at critical point, m\(^3\)kmol\(^{-1}\) \\
\( HC \) : hydrocarbon

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