

## ASSESSMENT OF REFRIGERANT MIXTURES PERFORMANCE WITH THERMAL GLIDE FOR COLD CLIMATE AIR-SOURCE HEAT PUMPS

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### ABSTRACT

Heat pumps are currently considered as one of the most promising means for meeting low energy consumption requirements in buildings. However conventional air source heat pumps suffer from severe limitations in terms of performance at low ambient temperatures, while new designs such as multi-stage compression or ground source heat pumps are still very costly. The main challenge is to improve on the air-source heat pumps low efficiency in cold climates at a reasonable cost. The use of mixtures of refrigerants with the aim of increasing heat pumps performance (COP and/or heating capacity) by taking advantage of the thermal glide has been so far, little studied for the heating and cooling of buildings. In this paper, the goal is to assess the performance of refrigerant mixtures with thermal glide for cold climate air-source heat pumps. A simple theoretical and an extended model have been developed and used for refrigerant mixtures performance evaluation. It is shown that a good potential exists in refrigerant mixtures with moderate glide to improve the performance of cold climate air-source heat pumps.

### INTRODUCTION

Heat Pumps (HPs) are a technology that can make a significant contribution to energy conservation. However, unlike fuel boilers or electric heaters, the efficiency of air-source HPs varies significantly with ambient temperature levels. When there is a high temperature difference between the cold source and the heat sink, the capacity and the Coefficient of Performance (COP) of the HP fall drastically. This is a major problem for air-source HP applications in cold climates.

Refrigerants as a means of transferring heat between heat sources and heat sinks have been widely used since Jacob Perkins in 1834 invented the first vapor-compression cycle.

Until the 1930s, the primary refrigerants used were ammonia, methyl chloride, and sulphur dioxide. Pictet in 1885 [1] applied a volatile liquid which could split-up into two or more volatile liquids; this can be considered as a first use of mixtures as a refrigerant. A more detailed literature review on refrigerants is presented by Calm and Didion [2].

The use of refrigerant mixtures to improve the performance of air-source HPs in cold climates is an option that has been little studied so far. Higher HP performance can be achieved by approaching the conventional heat pump cycle to the Lorenz cycle. More exactly for a fixed pressure conditions, a performance improvement is obtained by having the temperature variation during condensation and evaporation rather than the constant temperature in conventional cycles. This improvement is mainly reached by reducing heat transfer irreversibilities in the heat exchangers by reducing the thermal pinch. This will be obtained by having temperature glide in the heat exchangers through an appropriate selection of refrigerant mixtures. It is theoretically possible to produce a non-toxic and non-flammable (according to ASHRAE standard) mixture of refrigerants from existing classified pure refrigerants, corresponding exactly to the requirements of an application.

The main goal of the present study is to find a replacement refrigerant mixture that has a better performance in cold climates than common refrigerants. This replacement refrigerant must not only have a certain desirable thermophysical properties but also it should be nontoxic, non-flammable, oil soluble, have zero ODP and have a low GWP. Currently there is no acceptable pure refrigerant that satisfies all the required properties of a refrigerant [3]. Alternatively, by mixing two (binary) or more pure refrigerants, a desired working fluid might be obtained which may resolve the undesired properties of pure refrigerants by dilution. Therefore, refrigerant mixtures have the potential to provide the best

compromise for the pure fluids that meet some of the desirable properties of a required refrigerant. Refrigerant mixtures can be divided into three categories:

- I) Azeotropic refrigerant mixtures
- II) Near-azeotropic refrigerant mixtures
- III) Zeotropic (Non-azeotropic) refrigerant mixtures.

Azeotropic mixtures behave nearly like a pure fluid, i.e., under constant pressure they condense and evaporate at a constant temperature and the composition of the mixture in the vapor and the liquid phases is the same. Zeotropic mixture components have different mass fractions in the liquid phase and in the vapor phase at equilibrium condition. Therefore, a zeotropic mixture exhibits a significant temperature variation during constant pressure condensation and evaporation. At constant pressure, the difference between the saturated vapor temperature and the saturated liquid temperature is referred to as the "temperature glide" of the refrigerant. Near-azeotropic mixtures are mixtures with small temperature variation during condensation and evaporation and a small composition difference in liquid and vapor phases at equilibrium.

Azeotropic refrigerant mixtures have been traditionally used in HPs and refrigeration cycles. On the other hand, zeotropic refrigerant mixtures are used for specific applications. Works on refrigerant blends were made primarily for applications in cryogenics and in the replacement of CFCs. The best known works in cryogenics were produced in Russia in cooperation with the U.S. and led to a revolutionary single stage cryogenic refrigerator operating between 70K and 300K [4]. Zeotropic refrigerant mixtures offer certain advantages to the system:

- They can reduce the entropy generation in heat exchangers by glide matching.
- Their composition can be selectively varied on-line to meet the specific system requirements.

Over the past 20 years, the developments in the field of refrigerants has been limited to find suitable substitutes for CFCs in response to the Montreal Protocol and re-introduce natural refrigerants (ammonia, CO<sub>2</sub>) in response to the Kyoto Protocol. For example, Pannock and Didion [5] applied Cycle 11 model [6] to investigate the best possible binary zeotropic refrigerant mixture as the replacement of R-22 for residential HP applications. Rice [7] developed a simplified model called BICYCLE for simulation of pure and mixed refrigerants in order to evaluate the R-22 alternatives. Ragazzi and Pederen [8] studied the thermodynamic optimization of various evaporator designs with zeotropic refrigerant mixtures using an irreversibility-based function. Their main goal was to find a replacement for R-22. They showed that the zeotropic mixtures are less irreversible than the pure refrigerants with cross-counter-flow heat exchangers.

The use of mixtures of refrigerants with the aim of increasing the COP by taking advantage of large thermal glides has been little studied for household applications. That is the reason why the references cited in the current study are not very recent, as no significant activity has taken place recently in this area. In present study, it is aimed to investigate the possibility of using refrigerant mixtures in order to increase the performance of the HPs in cold climates by increasing the thermal glide. This study is performed in two phases. In phase I, a simplified screening HP model is used to study the performance of a group of selected refrigerant mixtures (only binary mixtures are considered) with different compositions. In phase II, the mixtures that were found to have a desirable performance in phase I will be studied with an extended model.

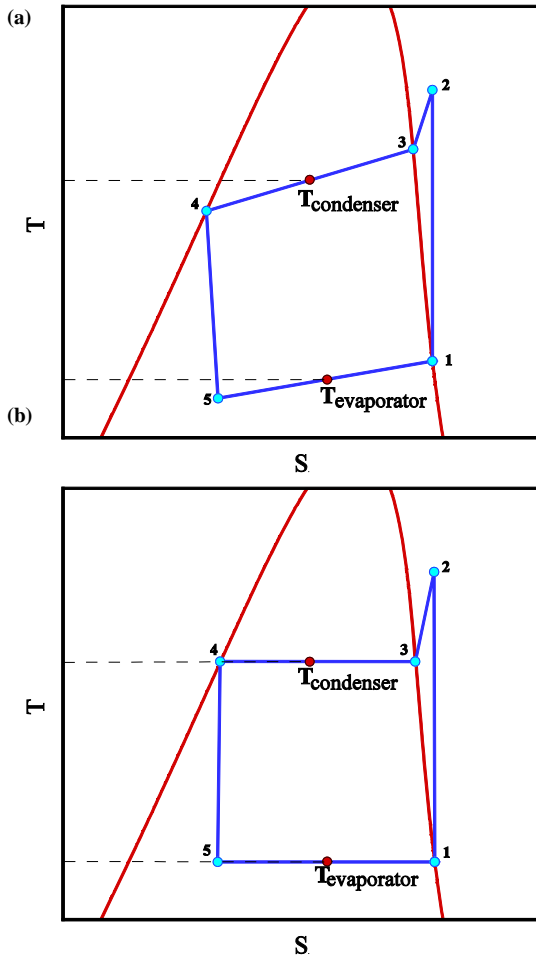
## THEORETICAL MODEL

As mentioned previously, in the first phase of this project a simplified model (theoretical cycle) for the HPs will be used to assess the thermal performance of the refrigerant mixtures. The Carnot cycle as an example of an idealized energy conversion cycle is of interest to researchers. However, the concept of the Carnot cycle is only (used in refrigeration applications) valid for the case of heat rejection and absorption at constant pressures and constant temperatures. A heat pump cycle with changing temperatures for the constant pressure heat rejection and absorption operates according to Lorentz cycle. The thermal efficiency of the cycles that work on constant heat sink and heat source temperatures (cycles that work on pure or azeotropic refrigerants) cannot exceed the efficiency of the Carnot cycle. However, an improvement in the efficiency of the cycles that work on refrigerants with temperature glide (cycles that work on zeotropic refrigerants) can be obtained by approaching the thermal efficiency of the Lorentz cycle.

In order to obtain meaningful results from the comparison of different refrigerant mixtures and pure refrigerants, a fair and conclusive calculation method is required. According to Ragazzi and Pederen [8], it is difficult to compare the Lorentz and Carnot cycle performance due to their different dependency on the evaporating and condensing temperatures. McLinden and Radermacher [9] presented a review of the methods for analytical comparison of pure and mixed refrigerants in vapor-compression cycles. They showed that the performance of the mixture relative to pure refrigerant is strongly dependant on how the equivalent temperature is determined in the heat exchangers. Comparing all the possible different cases for equivalent temperature, the case with constant average temperature for each phase change process seems to be the fairest case. Consequently, in this part of the project the comparisons are made according to constant average temperature. The Average Mean Temperature Difference (AMTD) as presented by Rice [7] is applied. In order to simplify the theoretical calculations, the following assumptions are made:

- The pressure losses and the heat losses to the environment are neglected.

- The isentropic compression and isobaric evaporation and condensation processes are assumed.
  - Refrigerant exits the condenser and evaporator as saturated liquid or vapour, respectively.
  - The expansion process is regarded as being isenthalpic.
- The T-S diagrams of the cycles used for the pure fluid and the mixtures are shown in Fig. 1.



**Figure 1** The T-S diagram of a theoretical heat pump cycle for: (a) Zeotropic mixture, and (b) Pure refrigerant

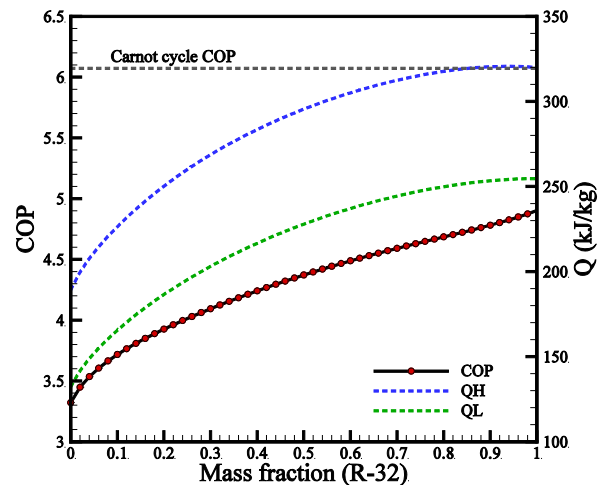
A computer code based on the theoretical heat pump model is developed [12] in the FORTRAN language. The NIST standard database, REFPROP version 9.0, is linked to the code to calculate the thermodynamic properties of the refrigerants and mixtures. The inputs of the code are the refrigerant components and their mass fractions in the mixture as well as the evaporator and the condenser working temperatures which are assumed to be  $-20^{\circ}\text{C}$  and  $30^{\circ}\text{C}$ , respectively.

## RESULTS

The results of the refrigerant mixtures studied are presented in three different groups corresponding small, moderate, and large glides. It should be noted that the glide is a characteristic of a given mixture, which does not change.

### Small glide (glide less than $10^{\circ}\text{C}$ )

Mixtures studied in this group include: R-134a/R-143a, R-134a/Propane, R-134a/I-butane, and R-32/ $\text{CO}_2$ . The latter mixture is taken as an example of the results obtained for mixtures with small glide, Fig. 2 presents the COP and heating capacity (heat delivered to the heat sink, QH and heat absorbed from the cold source, QL) as a function of fraction of R-32 in the mixture of R-32/ $\text{CO}_2$ . The obtained results show that, for the mixtures with small temperature glide, there is no improvement in the COP or the heating capacity (based only on the refrigerant properties). In other words, the COP and heating capacity of the mixture obtained is less than that of one of the pure components of the mixture. Therefore, mixtures with low glides are not of interest in the present study.



**Figure 2** COP and temperature glide of  $\text{CO}_2/\text{R-32}$

### Moderate glide (glide range of $10^{\circ}\text{C}$ - $40^{\circ}\text{C}$ )

Mixtures studied in this group include: R-134a/R-245fa, R-152a/R-245ca,  $\text{CO}_2$ /Propylene, R-134a/R-245ca, R-1234ze/Isopentane,  $\text{CO}_2/\text{R-1234yf}$ , Isopentane/R-1234yf,  $\text{CO}_2/\text{R-134a}$ ,  $\text{CO}_2/\text{R-134a}$ ,  $\text{CO}_2$ /Propane,  $\text{CO}_2/\text{R-152a}$ ,  $\text{CO}_2/\text{R-1234ze}$ , and  $\text{H}_2\text{S}/\text{Butane}$ . Figure 3 presents the COP and heating capacity as a function of fraction of R-134a in the mixture of R-134a/R-245ca as an example of the results obtained for mixtures with moderate glide. As can be seen, both the COP and the heating capacity of the mixture are slightly improved, from the pure refrigerants, for a range of mixture

combinations. The best COP is obtained for 134a/R-245ca (40/60), which is only 0.69% better than the COP for pure R-245ca. The best heating capacity is obtained for R-134a/R-245ca (30/70), which is 9.61% better than that of the R-245ca.

The obtained results for the mixtures studied with moderate temperature glide show that there is always an improvement in either or both of the COP and the heating capacity. Therefore, mixtures with moderate temperature glides are selected for further studies. By comparing all mixtures studied with moderate temperature glides, five mixtures are selected for further study (in Part II). These mixtures are: CO<sub>2</sub>/R-32 (10/90), R-134a/R245fa (33/64), CO<sub>2</sub>/R-134a (40/60), CO<sub>2</sub>/Propane (20/80), and CO<sub>2</sub>/R-152a (30/70).

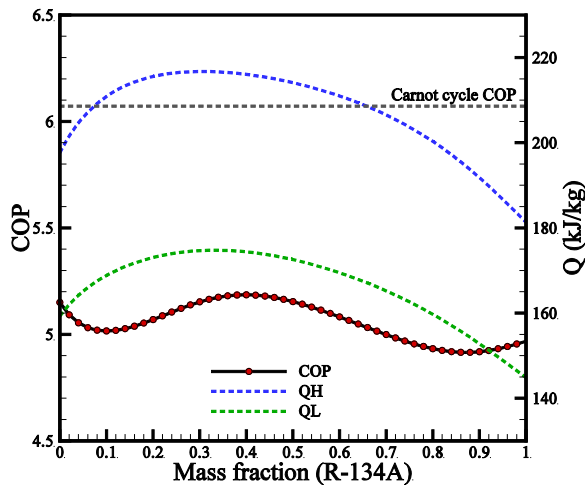


Figure 3 COP and temperature glide of R-134a/R-245ca

### Large glide (glide more than 50°C)

Mixtures studied in this group are: CO<sub>2</sub>/R-245fa, CO<sub>2</sub>/Butane, and CO<sub>2</sub>/R-245ca. Figure 4 presents the results obtained for CO<sub>2</sub>/Butane mixtures as an example. As is shown, an improvement is obtained in both the COP and the heating capacity. The best COP is obtained for the mixture of Butane/CO<sub>2</sub> (58/42), which is 7.25% and 68% better than the COPs for Butane and CO<sub>2</sub>, respectively. The evaporator and the condenser temperature glides for this mixture are 65.52°C, and 78.23°C, respectively. The best heating capacity is obtained for the mixture of Butane/CO<sub>2</sub> (82/18), which is 30.19% more than the heating capacity of Butane and 143.74% more than the heating capacity of CO<sub>2</sub>. The mixture of CO<sub>2</sub>/Butane may have desirable performance, but their corresponding temperature glide is very high. Such a high temperature glide causes the output temperature of the evaporator to be greater than the output temperature of the condenser. This situation is theoretically possible, but is not practical.

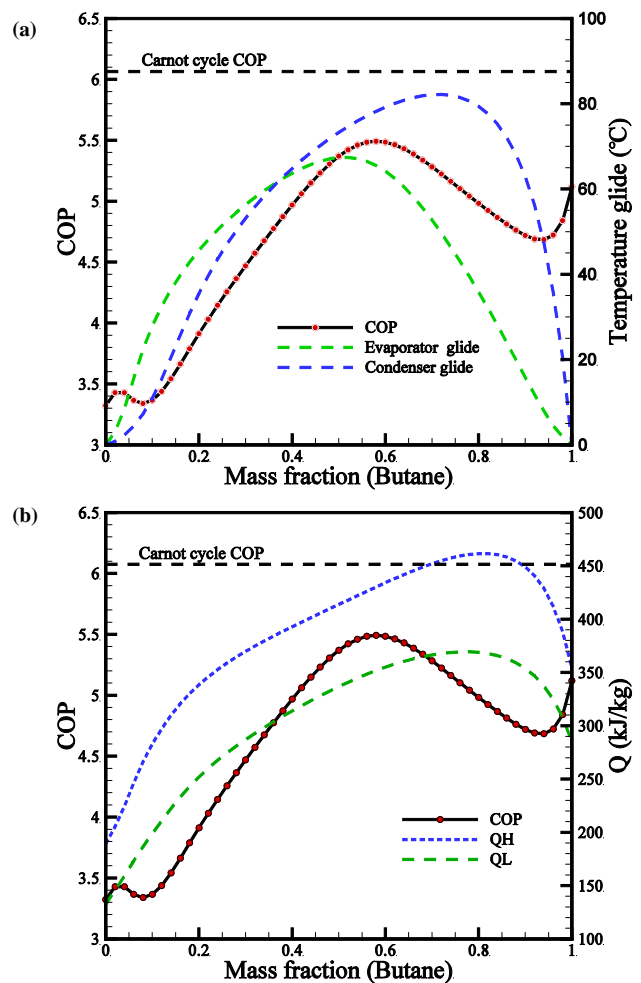


Figure 4 (a) COP and temperature glide; (b) COP and heating capacity; of Butane/ CO<sub>2</sub>

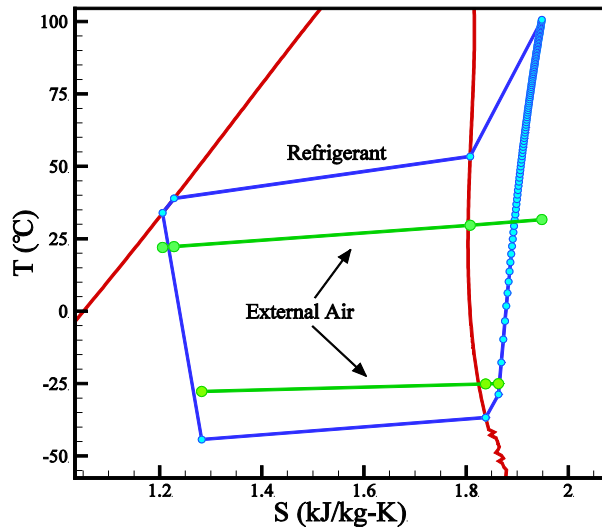
### EXTENDED MODEL

In the previous part of this study, different mixtures are compared based on a simple theoretical model; however, this kind of comparison is just based on the refrigerant temperature. In this part, refrigerant mixtures are studied with an extended model. In this model the following assumptions and modifications are considered:

- The compression process is polytropic, with constant polytropic efficiency.
- The Log-Mean-Temperature-Difference (LMTD) method is used for simulation of the evaporation and condensation processes.
- Air temperatures for evaporator and condenser are assumed to be constant [3].
- Constant air flow rates are considered for heat exchangers.
- UA (the product of the overall heat transfer coefficient and a heat transfer area in the heat exchangers) is assumed to be constant [10].

- The pressure losses are assumed to be constant for different refrigerants.
- Refrigerant exiting the condensers and evaporators are subcooled and superheated, respectively.
- The expansion process is regarded as being isenthalpic.

These assumptions are applied on all mixtures and pure refrigerants simulated in order to have a fair comparison.



**Figure 5** T-S diagram of the improved model heat pump cycle for R-134a/R245fa (33/67)

The corresponding computer code is also developed in the FORTRAN language and the NIST standard database, REFPROP version 9.0 is linked to the code to calculate the thermodynamic properties. Inputs of the code are presented in Table 1. Figure 5 shows the T-S diagram of the improved model HP cycle for R-134a/R245fa (33/67).

## RESULTS

Currently, R-410a is one of the common refrigerants used in HPs. Therefore, in this study R-410a will be used as a reference refrigerant in order to compare the performance of new refrigerant mixtures. As mentioned before, here the performance of five different mixtures chosen in Sec. 2.1.2. (CO<sub>2</sub>/R-32 (10/90), R-134a/R245fa (33/64), CO<sub>2</sub>/R-134a (40/60), CO<sub>2</sub>/Propane (20/80), and CO<sub>2</sub>/R-152a (30/70)) are compared. Figure 6 presents (a) COP; (b) heating capacity; (c) compressor pressure ratio; and (d) evaporator pressure as a function of the outdoor air temperature. As can be seen, while the pure refrigerants R-134a and propane have the best COPs, the heating capacity of all five mixtures are better than those of the pure refrigerants and even R-410a. Among the mixtures studied, R-134a/R245fa (33/67) has the best COP and heating capacity; however it has the highest compression ratio and the lowest evaporator pressure. By adding another pure refrigerant to this mixture, it may be possible to reduce its high pressure ratio and increase its low evaporator pressure (above atmospheric pressure) while keeping its good thermal performance. Moreover, CO<sub>2</sub>/R-152a and CO<sub>2</sub>/Propane have good heating capacities and better compression ratios and

evaporator temperatures. From what is shown here, it can be concluded that zeotropic refrigerant mixtures have good potential to improve the performance of HPs in cold climates; however, more research is required in this area in order to find the most suitable mixture.

## CONCLUSION

In this study, zeotropic refrigerant mixtures are evaluated for use in cold climate air-source heat pumps. Different refrigerants are screened by a simple theoretical model and then five mixtures are selected for further studies with a modified model. The results obtained show the potential of zeotropic refrigerant mixtures with moderate glide to have a better performance than pure refrigerants in cold climates. Further studies are required to assess their performance more accurately. According to Hogberg et al. [11], the most accurate method of comparison of zeotropic refrigerant mixtures is assuming equal heat transfer area; however, this approach is more rigorous and requires the detailed modeling of the heat transfer and pressure drop in the evaporator and condenser. Studying the performance of zeotropic mixtures with such an advance model would be the next step of this project.

## ACKNOWLEDGEMENTS

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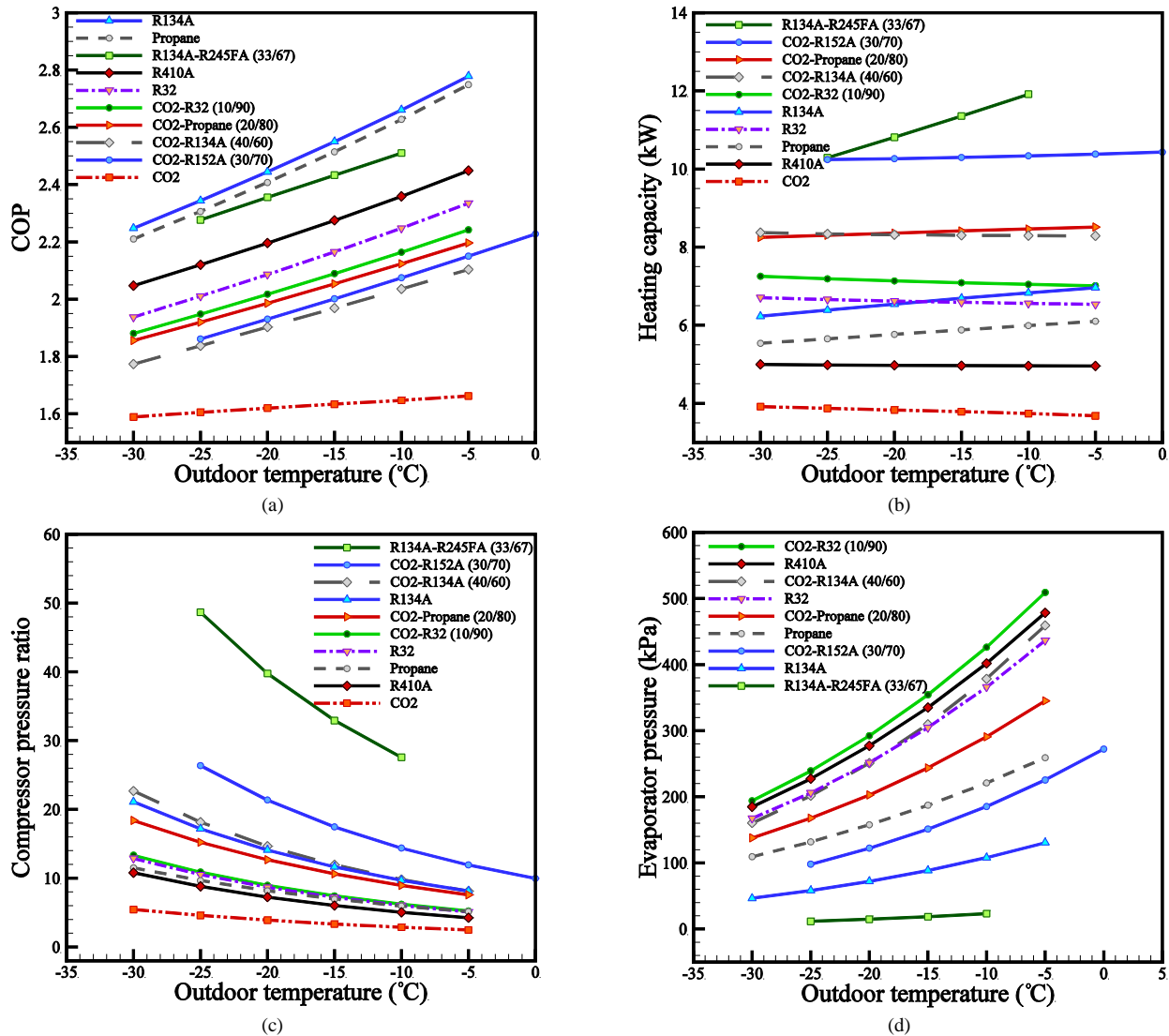
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**Table 1.** Simulation inputs for the extended model

Condenser air temp.	Evaporator /Condenser UA	Condenser superheat UA	Evaporator superheat temp.	Condenser Subcooling temp.	Condenser pressure drop	Evaporator pressure drop	Evaporator air flow rate	Condenser air flow rate
22 °C	300J/K	50J/K	8 °C	5 °C	6kPa	0.3kPa	1.5m <sup>3</sup> /s	0.9m <sup>3</sup> /s



**Figure 6.** (a) COP; (b) heating capacity; (c) compressor ratio; and (d) evaporator pressure as a function of outdoor air temperature.