CHEMICAL ENGINEERING TRANSACTIONS
VOL. 94, 2022
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Petar S. Varbanov, Yee Van Fan, Jiří J. Klemeš, Sandro Nižetić

ISBN 978-88-95608-93-8; **ISSN** 2283-9216
DOI: 10.3303/CET2294198

Use of Refrigerant Blends to Improve Thermal Efficiency of Heat Pump Cycles

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High temperature heat pumping (HTHP) is a key technology for minimising emissions from industrial process heat. One option for improving thermal efficiency in heat pump cycles is to match temperature profiles of the refrigerant with the heat source and heat sink fluids as closely as possible. For a pure chemical species evaporation occurs essentially at constant temperature, making it difficult to match the temperature profiles of the refrigerant and heat source fluid. However, the evaporation process for refrigerant mixtures occurs over a range of temperatures, and this range can, within limits, be customised for a particular process. This study describes the development of a heat pump model implemented in Python (checked against data generated in Aspen HYSYS) that was used to investigate whether binary mixtures of alkanes are capable of yielding higher COPs and higher exergy efficiency values when compared to each alkane in its pure form as a result of reduced exergy destruction. A general trend for all mixtures was that COP and second-law efficiency were maximised when the mass fraction of the smaller molecule was between 0.1 and 0.3. It was also observed that the trend was magnified when the difference in boiling points between the two constituents increased. For a heat source glide between 35 °C and 40 °C and a heat sink glide between 40 °C and 80 °C, a mixture of 17 % propane and 83 % pentane gave the highest COP of 4.5 and the highest exergy efficiency of 44.7 %.

1. Introduction

In the push toward achieving carbon neutrality, one area that poses a particular challenge is industrial process heating where much of the heat still comes from fossil fuel combustion (Thiel and Stark, 2021). Heat pump technology offers low-emission process heat options suitable for a range of industries and is much more energy-efficient than direct electrode or ohmic heating (Arpagaus et al., 2016). However, most commercial heat pump technology is limited to heat sink outlet temperatures below 100 °C, and while this is suitable for a range of applications, (e.g. hot water for hygienic cleaning in the food industry), there are many applications that require temperatures significantly above 100 °C. Higher temperatures are associated with higher refrigerant pressures which can stretch the capability of many current designs; however, despite these challenges, a number of prototype designs have reached temperatures reported to be in the region of 160 °C (Jesper et al., 2021). Another challenge lies in the efficiency limitations of pure substances. Most refrigeration and heat pump cycles make use of pure substances as refrigerants. These fluids undergo an isothermal phase change in the evaporator and condenser, which is shown graphically by a flat line on a temperature-enthalpy (T-H) chart. The temperature profiles of pure substances often match poorly with that of the heat transfer fluids in both exchangers, which results in significant exergy destruction in the heat exchange process. Zeotropic mixtures on the other hand, experience a temperature glide during phase change. This phenomenon can be applied to vapour compression cycles to align the temperature profile of the refrigerant to that of the heat transfer fluids, resulting in a higher exergy efficiency and a higher COP (Zühlsdorf et al., 2018). An alternative approach is to use gas-phase refrigeration such as the Joule cycle (or reverse Brayton cycle) to generate temperature glide on both sides of the heat pump (Gai et al., 2019). However, Joule cycle heat pumps in practice are rare due to the need for very high efficiency compression and expansion.

Paper Received: 10 May 2022; Revised: 21 June 2022; Accepted: 21 June 2022
Please cite this article as: Taylor J.J., Carson J.K., Hoang D.K., Walmsley T.G., Chen Q., Cleland D.J., 2022, Use of Refrigerant Blends to Improve Thermal Efficiency of Heat Pump Cycles, Chemical Engineering Transactions, 94, 1189-1194 DOI:10.3303/CET2294198

The aim of this study is to examine how the performance of a single-stage heat pump cycle is affected by binary zeotropic blends of refrigerants compared to a pure species refrigerant under the same conditions. The family of n-alkanes were chosen for investigation since mixtures of alkanes behave ideally (Smith et al., 2005), they are natural refrigerants and have minimal impact on the climate and atmosphere, and the thermodynamic properties (critical point, triple point, saturation curves etc.) of the alkanes vary nearly monotonically with increasing molecular size. There does not appear to be any study in the open literature that has identified optimum blends (in terms of maximum COP) for the family of n-alkanes.

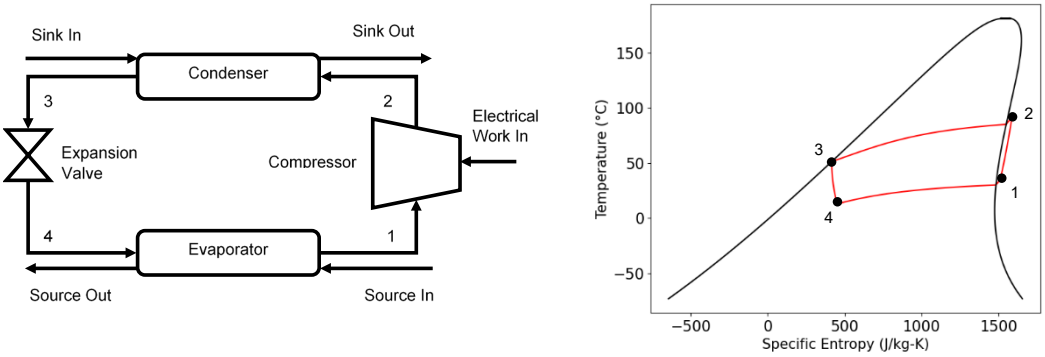
2. Methods

2.1 Thermodynamic model

A thermodynamic model of a heat pump cycle was implemented, as shown in Figure 1. The refrigerant is evaporated and superheated by receiving heat from the heat source at low pressure in the evaporator (4-1), before compression in the compressor (1-2) followed by rejection of the heat to the heat sink stream in the condenser at higher pressure and temperature (2-3). The fluid then expands (3-4) to low temperature and pressure, before it absorbs heat again.

The following assumptions were made to create the heat pump model:

- Steady-state operation
- Isenthalpic expansion
- Isentropic compression efficiency: $\eta_{is,\,comp}$ = 70 %, $\eta_{me,comp}$= 100 %
- Isobaric heat transfer processes
- Pinch point temperature difference: $\Delta T_{pinch,\,eva} = \Delta T_{pinch,\,cond}$ = 5 °C
- Heat source: $\dot{m}_{source}$ = 1 kg s^{-1}, $T_{source,\,IN}$ = 40 °C, $T_{source,\,OUT}$ = 35 °C
- Heat sink: $T_{sink,\,IN}$ = 40 °C, $T_{sink,\,OUT}$ = 80 °C



(a) *(b)*

Figure 1: Plot of a) Cycle diagram and b) T-s diagram of the system

The refrigerant leaving the evaporator was modelled as superheated vapor with 5 °C superheat, T_{SH} = 5 °C, to avoid condensation in the compressor ("wet compression"). The condensing pressure was calculated based on a saturation temperature that is always 5 °C higher than the outlet temperature of the heat sink fluid, and a quality of 1.

The heat pump cycle is characterised by determining the state points of the working fluid using the energy balance at each component as below:

Evaporator: $$\dot{Q}_E = \dot{m}_{source}\left(h_{source,in} - h_{source,out}\right) = \dot{m}_{ref}(h_1 - h_4) \quad (1)$$

Condenser: $$\dot{Q}_C = \dot{m}_{sink}\left(h_{sink,\mathrm{out}} - h_{sink,in}\right) = \dot{m}_{ref}(h_{2,ac} - h_3) \quad (2)$$

Compressor: $$\dot{W}_C = \dot{m}_{ref}\left(h_{2,ac} - h_1\right), \quad \text{where } h_{2,ac} = h_1 + \frac{h_{2,is} - h_1}{\eta_{is}} \quad (3)$$

Expansion valve: $$h_3 = h_4 \quad (4)$$

The thermodynamic model was implemented in Python with fluid properties obtained from REFPROP (Lemmon et al., 2013). A script was created that allowed the user to input the heat source and heat sink inlet and outlet temperatures. It also allowed the user to select two n-alkanes from propane, butane, isobutane, pentane, hexane, and heptane to be used in a refrigerant blend. The alkane mixtures were assumed to obey Raoult's Law (Smith et al., 2005). The Python script simulated the model for various mixtures of the two selected pure substances. This process was iterated for every mixture combination with the mass fraction of component increased by 1 % for each step.

Heat exchangers were modelled by discretising the heat exchanger into 100 nodes, and calculating the temperature change each fluid experiences as it passes through each node. If the two fluids produced a temperature cross at any node in any heat exchanger, the mixture was invalidated and removed from comparisons with other mixtures. In most cases a minimum temperature approach of 5 °C was achieved.
Figure 2 shows a comparison of the results for a mixture of n-butane and n-hexane from the Python model against results from simulations performed under the same conditions and using the same modelling approach in Aspen-HYSYS™, which is a widely used simulation tool of industrial chemical and process engineering applications (Ali et al., 2021). The Peng-Robinson property package in Aspen-HYSYS™ was selected. The close agreement between the two sets of data serves as a check of the Python model.

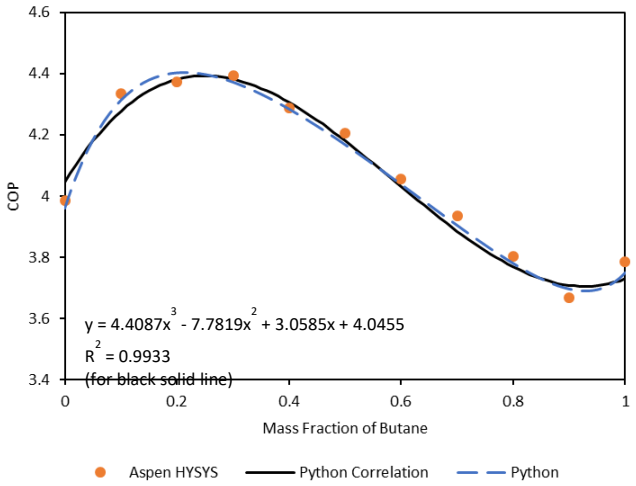


Figure 2: Comparison between the Python model results, and the Aspen HYSYS results for different blends of n-butane and n-hexane. A correlation equation is provided for the Python model results with an R^2 value

2.2 Thermodynamic performance evaluation

The thermodynamic performance of the heat pump cycle then can be analysed based on different performance indicators. The COP relates the condensing heat flow, $\dot{Q}_C$ to the consumed electric power of the compressor, $\dot{W}_c$

$$COP = \frac{\dot{Q}_C}{\dot{W}_C} \tag{5}$$

The Lorenz COP is the maximum theoretical COP that can be achieved when the heat source and heat sink have variable temperatures. The Lorenz COP depends on the temperatures of both streams, and it is calculated as follows using absolute temperatures.

$$COP_{Lorenz} = \frac{T_{sink,av}}{T_{sink,av} - T_{source,av}} \tag{6}$$

$$T_{sink,av} = \frac{T_{sink,out} - T_{sink,in}}{\ln\left(\frac{T_{sink,out}}{T_{sink,in}}\right)}, \quad T_{source,av} = \frac{T_{source,in} - T_{source,out}}{\ln\left(\frac{T_{source,in}}{T_{source,out}}\right)} \tag{7}$$

The exergy efficiency ε accounts for the exergy of the streams and is defined as Eq. (8) (Zühlsdorf et al., 2018) considering a dead state at conditions of T_o = 20 °C and P_o = 101.325 kPa

$$\varepsilon = \frac{\dot{X}_{sink,out} - \dot{X}_{sink,in}}{\dot{X}_{source,in} - \dot{X}_{source,out} + \dot{W}_C} \times 100\ \% \tag{8}$$

The exergy of a stream, $\dot{X}$, is defined as the maximum work, which can be obtained from a stream while it is brought from the initial state into thermodynamic equilibrium with the environment, as determined by Eq. (9):

$$\dot{X} = \dot{m}(h - h_0 - T_0(s - s_0)) \tag{9}$$

where h and s are the specific enthalpy and specific entropy of the stream at the initial state and h_o and s_o are the specific enthalpy and specific entropy at the dead state. In real processes, exergy is always destroyed due to entropy generation that arises because of irreversibility in the system. The exergy balances for each component in the heat pump cycle may be calculated as follows.

$$\dot{X}_{destroyed,evap} = \dot{m}_{ref}(x_4 - x_1) + \dot{m}_{source}(x_{source,in} - x_{source,out}) \tag{10}$$

$$\dot{X}_{destroyed,comp} = \dot{W}_C + \dot{m}_{ref}(x_1 - x_2) \tag{11}$$

$$\dot{X}_{destroyed,cond} = \dot{m}_{ref}(x_2 - x_3) + \dot{m}_{sink}(x_{sink,in} - x_{sink,out}) \quad (12)$$

$$\dot{X}_{destroyed,exp} = \dot{m}_{ref}(x_3 - x_4) \quad (13)$$

When performing an exergy balance across the compressor, the exergy from the work coming into the compressor equals the work itself. The total exergy destruction of the cycle is calculated by adding together the exergy destruction values from all four components in the cycle.

Second-law efficiency is finally calculated according to Eq. (14):

$$\eta_{II} = \frac{COP}{COP_{Lorenz}} \times 100\ \% \quad (14)$$

3. Results and discussion

An example of the temperature profiles of the refrigerant and the heat transfer fluid for both the evaporator and condenser are shown in Figure 3. The refrigerant was a mixture of 17 % propane and 83 % pentane on a mass basis. The mass fractions of the two components have been selected to optimise temperature matching with the source and sink fluids in order to minimise exergy destruction and maximise COP. This illustrates how the Python tool may be used to select refrigerants for optimal heat transfer efficiency for given source and sink target temperatures. With the addition of fluid-phase equilibrium calculation capability for non-ideal solutions, the Python model could be extended to include other refrigerants, and it could also be adapted to incorporate other heat pump cycle features components such as multi-staging, internal heat exchangers etc.

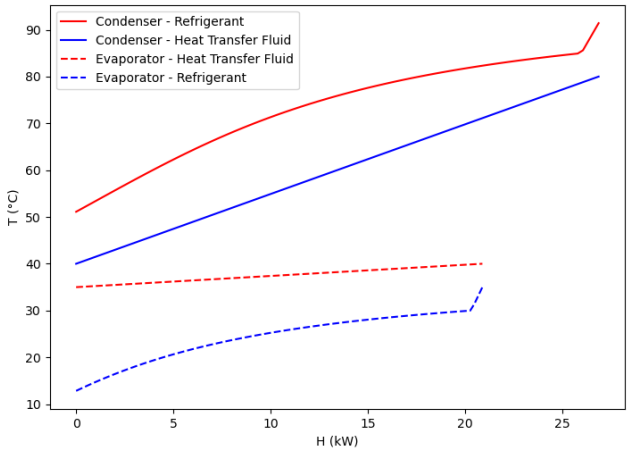
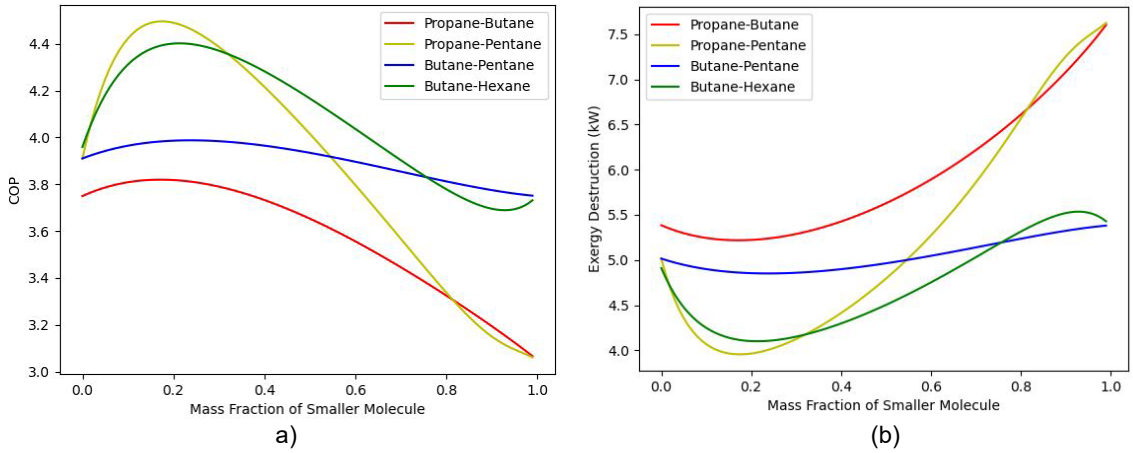


Figure 3: Temperature versus enthalpy diagram for the refrigerant (17 % propane, 83 % pentane by mass) and the heat source and sink fluids in the evaporator and condenser

Figure 4 shows the COP as a function of the mass fraction of the smaller component for selected binary mixtures of n-alkanes, where for all blends considered the mixture COP had a dependence on the blend composition.



a) (b)

Figure 4: COP changes (a) and total exergy destruction changes (b) as the mass fraction of the smaller molecule changes for four groups of mixtures

All mixtures in Figure 4 obeyed the minimum temperature difference requirement. Figure 4 demonstrates that binary n-alkane mixtures can, according to the Python model, increase the performance of subcritical vapour compression cycles when compared to systems operating with pure n-alkanes. The maximum COP was achieved when the smaller molecule in the mixture had a mass fraction between 0.1 to 0.3, and the variation in COP with composition increased as the difference in molecular size between the components increased. As would be expected, the trend in the exergy destruction mirrored that of the COP, in that an increase in the COP corresponded to a decrease in the exergy destruction, and vice versa.
Figure 5 depicts the temperature glide of each mixture type as a function of the mass fraction of the smaller molecule. Greater temperature glides could also be achieved with increasing differences in molecular size due to the increasing difference in critical temperatures.

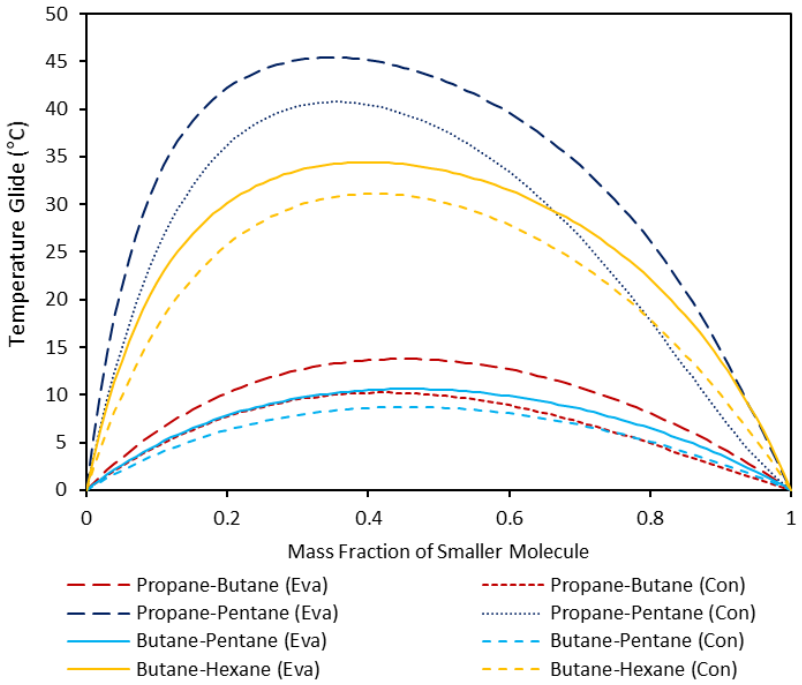


Figure 5: Temperature glides of each mixture type as the mass fraction of the smaller molecule changes

Table 1 shows a summary of the COP, exergy efficiency, and second-law efficiency for the best-performing mixtures, as well as key operating conditions for the test case. The mixture of 17 % Propane and 83 % Pentane shows the best result for all the performance indicators at moderate operating pressures (P_{eva} = 108 kPa and P_{cond} = 511 kPa) and low volumetric flow rate (0.023 m^3/s).

Table 1: Summary of key performance metrics and operating conditions for all best-performing mixtures

Mixture Type	Best-Performing Blend	COP	η_{II}(%)	ε (%)_	$\dot{m}_{ref}$ (kg/s)	$\dot{V}_{suction}$ (m^3/s)	P_{evap} (kPa)	P_{cond} (kPa)
Propane/Butane	0.17/0.83	3.8	25.4	39.2	0.089	0.011	338	1,332
Propane/Pentane	0.17/0.83	4.5	29.9	44.7	0.066	0.023	108	551
Butane-Pentane	0.24/0.76	4.0	26.5	40.6	0.083	0.029	103	511
Butane-Hexane	0.21/0.79	4.4	29.2	44.0	0.069	0.066	33	220

4. Conclusions

A model for a single-stage heat pump was developed in Python and checked against simulations from Aspen HYSYS. The model was used to investigate how binary mixtures of n-alkanes could be customised to better match the temperature profile of the refrigerant with that of the source and sink fluids in the evaporator and condenser. It was observed that the simulated COP and exergy destruction had a strong dependence on the relative amounts of the two components in the refrigerant mixture, with a maximum COP occurring typically with mass fractions of 0.1 to 0.3 of the lighter n-alkane in the blend. It was also observed, as was expected, that

larger temperature glides could be achieved with blends of n-alkanes differing by more than one carbon atom. For a heat source glide between 35 °C and 40 °C and a heat sink glide between 40 °C and 80 °C, a mixture of 17 % propane and 83 % pentane gave the highest COP of 4.5 and the highest exergy efficiency of 44.7 %.

Nomenclature

h - the specific enthalpy of the fluid, kJ kg^{-1}
$\dot{m}$ – mass flow rate, kg s^{-1}
s - specific entropy of the fluid, kJ kg^{-1} K^{-1}
x - specific exergy of the fluid, kJ kg^{-1}
η – compressor efficiency
$\dot{W}_c$ – work, kW
P – pressure, kPa
$\dot{Q}$ – heat duty, kW
T- temperature, K or °C

Subscript
1,2,3,4 – position of refrigerant in the heat pump cycle
ac – actual
av – average
C - condenser
E- evaporator
o – dead state
ref - refrigerant
is - isentropic
SH – super heat

Acknowledgements

This research has been supported by the programme “Ahuora: Delivering sustainable industry through smart process heat decarbonisation”, an Advanced Energy Technology Platform, funded by the New Zealand Ministry of Business, Innovation and Employment.

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