Approximation of Vapor Pressure Curve with Optical Methods in a Heat Pump Test Stand for Pure Isobutane and an Isobutane/Propane Mixture

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ABSTRACT

A reliable description of the dew line of refrigerants is paramount for the safe operation of heat pumps. For commonly used molecules in industrial heat pumps, dew point temperature data for the control of effective superheat are widely available and can be cast into empirical correlations as needed. However, the approach to customize refrigerant mixtures has gained attention in recent years, which introduces a need to find empirical correlations to describe the vapor pressure curve for a wide range of fluid mixtures, for which there is no experimental data available yet. This study searches for dew point temperatures by manually controlling the opening of the expansion valve such that trace amounts of liquid can be detected at the evaporator outlet through a sight glass. Detection is possible through visual inspection of the sight glass or through a low-cost optical sensor. Both methods are compared for pure R-600a and a mixture of R-600a and R-290. For pure R-600a, the best polynomial could reproduce the reference vapor pressure curve within the valid temperatures with a maximum deviation of $12.3\ kPa$ $(1.2\ K)$. For the mixture, the best fit achieved an accuracy of $56.5\ kPa$ $(3.4\ K)$. The demonstrated approaches to measure saturated gas pressures have proven to produce saturated gas properties within the upper limits of accuracy that can be found in literature while being significantly less complex. Especially the detection of liquid droplets in the sight glass based on diode voltage shows potential for systematic development, for example for accelerated characterization of refrigerant properties or direct superheat control.

1. INTRODUCTION

Recent studies have proven experimentally that the performance of heat pumps with high temperature differences in source and/or sink can be improved by utilizing the temperature glide of zeotropic fluid mixtures (Brendel et al., 2024). Although this is promising for the electrification of process heat, secondary problems arise for the operation of heat pumps with mixtures that are not sufficiently characterized or problems like composition shifts arise. For commonly used molecules like R-717 or R-290, empirical correlations can be fitted for the control of the expansion valve by using available data bases. Fitting the coefficients of these empirical correlations depends on data for the vapor pressure, which can be obtained in multiple ways for customized refrigerant blends. One approach could be to utilize common libraries for the calculation of those dew lines, like CoolProp or REFPROP (Bell et al., 2014; Lemmon et al., 2018). The accuracy of mixture predictions with REFPROP relies on the quality of the reference equations of state and the availability of mixture models for the desired combination of molecules (Lemmon et al., 2018). Considering the number of available molecules, therefore the number of possible combinations, and the experimental effort to find reliable mixture models, this could be a roadblock for projects with short timelines. For example, McLinden and Richter demonstrated an approach to directly measure dew line pressures and temperatures with a two-sinker apparatus (McLinden & Richter, 2016). Their technique delivered highly accurate dew point properties for a methane – propane system, however, the operation of elaborate setups linker a two-sinker apparatus requires substantial amounts of training and resources. This contribution investigates two alternative approaches to collect data from which a polynomial for the vapor pressure curve can be fitted. Both methods are tested in a heat pump test stand, utilizing a sight glass after the evaporator. First, the sight glass was manually observed by the operator to reproduce a spraying phenomenon (Brendel et al., 2024b). The second method relied on the observation of the voltage of a clip-on photo-diode sensor, which depends on a light source and the reflectiveness of the bottom of the sight glass (Schindler et al., 2023). Both methods were tested with pure R-600a and a mixture of R-600a with 40 $\%_m$ of R-290. It was evaluated how close the measured pressure and temperature combinations compare to the saturation pressures according to REFPROP.

2. METHODOLOGY

The experimental setup is published in this configuration for the first time in 2023 and is shown in Figure 1 (Brendel et al., 2023). Prior work delivers experimental results on zeotropic mixtures with synthetic refrigerants and hydrocarbons, with sink temperatures up to 150 °C, temperature differences in heat sink and heat source up to 35 K, and refrigerant temperature glides up to 40 K (Brendel et al., 2024). The effective superheat is controlled with an electronic expansion valve (EXV), via a PID controller or manual setting of the opening degree. An internal heat exchanger (IHX) is installed after the evaporator to provide additional superheat, which is essential for the present experiments, as set points are intended to be close to the dew line and liquid droplets at the evaporator outlet are intended. A suction line accumulator serves as redundancy for additional compressor safety.

Experiments are recorded first for pure R-600a. The mixture with R-290 is created by adding the refrigerant and tracking the mass using a scale. This mixture is sufficiently characterized in REFPROP and is therefore a suitable reference mixture to test the proposed method (Kunz & Wagner, 2012). Previous studies with the same heat pump have shown that the circulating composition was mostly within ± 0.03 to the charged composition for the mixtures R-290/R-600 and R-290/R-601 (Brendel et al., 2024b). Although the particular pair of R-290 and R-600a was not included in these tests, this study assumes that the circulating composition equals the charged composition.

The desired operating points are achieved as follows. The source is set to the desired set point by balancing the capacity of the electric heater and regenerator with the opening degree of the three-way valves. The system is then stabilized at the desired source temperature with a stable effective superheat of 7 K, where the superheat was calculated from the temperature difference between the measured evaporator outlet temperature and the REFPROP prediction of saturation temperature at the measured evaporator outlet pressure, for both R-600a and the R-600a/R-290 mixture. Large mass flows are applied at the source to reduce the influence of heat pump fluctuations on the source set point.

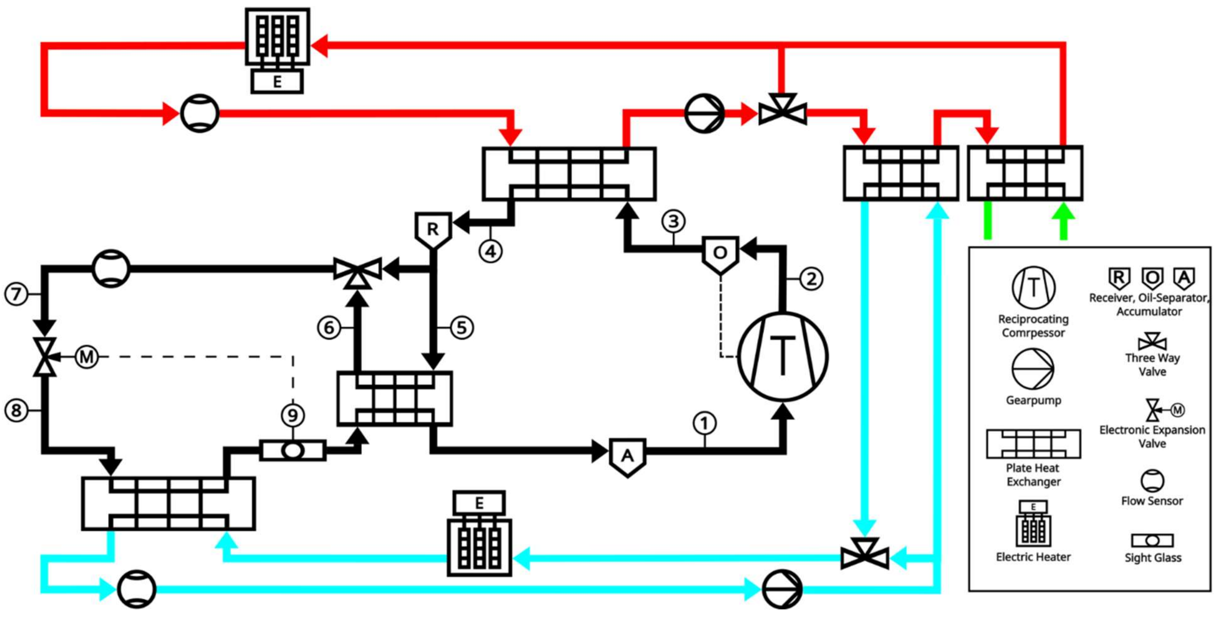

Figure 1: Simplified P&ID-scheme of heat pump with source and sink configuration (L. Brendel et al., 2023)

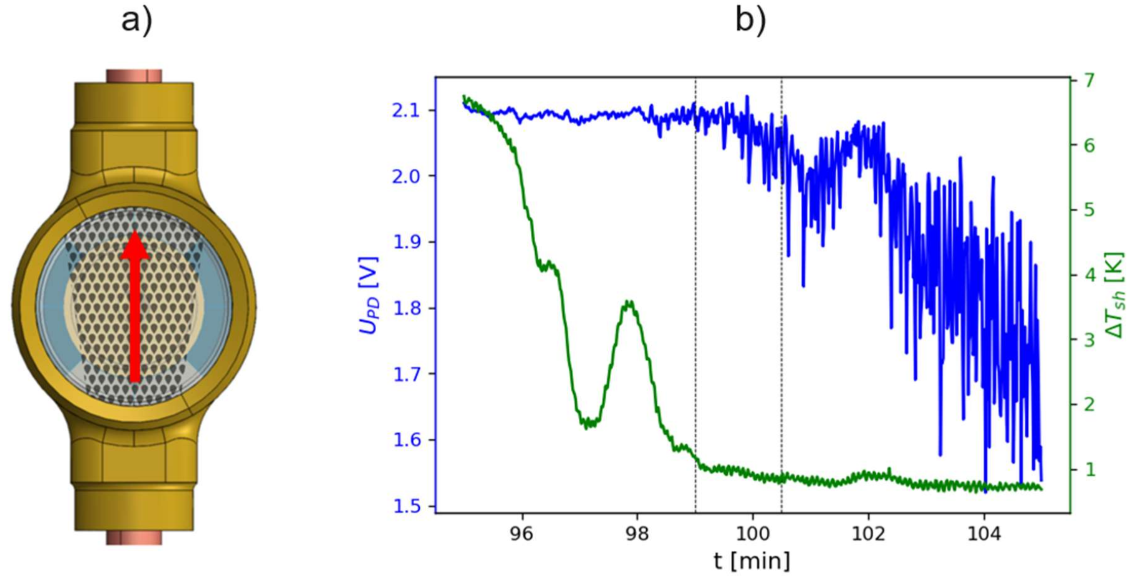

Figure 2: a) Schematic representation of the desired spraying phenomenon to set evaporator outlet close to saturated vapor b) U_{PD} and ΔT_{sh} when evaporator outlet approaches saturated vapor

The opening degree of the EXV is subsequently switched to manual control and gradually opened until a non-continuous, fog-like spraying, is observed. The system is then held steady for 60 seconds to record pressure and temperature at a stable EXV opening degree. This procedure is carried out for sink inlet temperatures between 20 °C and 60 °C in 10 K steps for all four test cases.

Sight glass observations are conducted using two methods, which are schematically presented in Figure 2. A spraying phenomenon, where a mist of small, liquid refrigerant droplets appears in the sight glass, was interpreted as the state of the evaporator outlet being close to saturated vapor. The appearance of this spraying phenomenon is shown in Figure 2 a), and a video recording can be obtained from the corresponding author. The first method relies on manual observation of the sight glass by the operator to identify the spraying phenomenon. (Brendel et al., 2024a). The second method relies on monitoring the voltage of a photo-diode (U_{PD}). An LED shines through the sight glass, reflects off its bottom surface, and excites a voltage in the photo-diode. The voltage remains stable at a value specific to the diode when pure gas is present in the sight glass. The presence of liquid droplets alters the reflectiveness, causing the voltage to drop and oscillate (Schindler et al., 2023). Figure 2 b) shows a plot of the voltage of the photo diode, U_{PD}, and the effective superheat ΔT_{sh} over time for an experiment with pure R-600a. Within the indicated time-window, ΔT_{sh} approaches a minimal value and at the same time, U_{PD} starts to drop and oscillate. The desired behavior of U_{PD} was determined by repeatedly monitoring the voltage and observing the sight glass manually until the appearance of U_{PD} was identified that corresponded with the desired spraying phenomenon.

The results are compared to REFPROP predictions of saturation pressure at the measured temperatures. The metric used is the relative deviation of the recorded pressure from the REFPROP saturation pressure, δ_{rel}, according to Equation (1), where T_9 and p_9 are the temperature and pressure measured directly after the sight glass.

$$\delta_{rel} = \frac{(p_9 - p_{sat,REFPROP}) * 100}{p_{sat,REFPROP}} \text{ with } p_{sat,REFPROP} = p(T_9, Q = 1, \text{Fluid}) \quad (1)$$

REFPROP saturation pressures are obtained by calling the REFPROP backend through CoolProp, using the measured temperatures and defining a quality of 1(Bell et al., 2014; Lemmon et al., 2018).

An empirical correlation is fitted to the measured pressure and temperature combinations using the equation employed in-house at OST, see equation (2). Three coefficients, c_1, c_2, and c_3, are optimized for each of the four datasets using the *curve_fit* function of the *scipy.optimize* package with default settings (Virtanen 2020).

$$p_{sat} = c_1 + c_2 * T^{0.5} + c_3 * T^{0.3} \quad (2)$$

3. RESULTS AND DISCUSSION

3.1. Pressures Relative to REFPROP Vapor Pressure Curve

The relative deviation δ_{rel} for all four datasets is shown in Figure 3. For pure R-600a, the measured pressures are within 4 % of the REFPROP saturation pressures. Neither dataset shows a trend with increasing evaporation pressure, and neither method (visual inspection nor optical measurement) proves more precise than the other. Both methods exhibit notable random scatter and consistently underpredict saturation pressures across all set points. For reference, literature reports saturation pressures for pure R-600a within 0.2 % of reference data using dedicated metal-bellows variable volumeters (Miyamoto et al., 2004). For the mixture, saturation pressures are underpredicted by between 7 % and 13 % compared to REFPROP mixture models. The method based on diode voltage yields consistent underpredictions of around 10 % with one measurement at approximately -7%, while the manual method shows a trend toward larger underprediction as evaporation pressure increases. Literature values for natural gas mixtures report deviations of between 5 % and 15 %, placing both methods at the upper limit of what is achieved with dedicated setups (McLinden & Richter, 2016). More elaborate approaches like the measurement of dew line pressures with a two-sinker presented by McLinden et. al. achieve an agreement within 3 % of reference equations of state (McLinden & Richter, 2016). Several factors likely contribute to the observed deviations, given the heuristic nature of both approaches and the fact that the experimental setup is not specifically designed for these measurements. The spraying condition cannot be maintained for more than 60 seconds and the temperature is measured on the outside of the tube, making it unlikely that thermal equilibrium is reached within the time of observation, such that the measured temperature probably does not reflect the actual fluid temperature. For the mixture, additional complications arise from the differences in boiling points of the components. The more volatile component boils off first, meaning that the liquid droplets observed in the sight glass are unlikely to have the same composition as the fluid charged into or circulating in the heat pump. As a result, the relative deviation with respect to the REFPROP vapor pressure is expected to be larger than what is observed for pure R-600a. Implementing this method in a test rig without oil, measuring the temperature in-line and using higher accuracy instrumentation would likely improve the results. Beyond these physical considerations, the heuristic nature of both methods must be acknowledged: The presented data is difficult to reproduce. Nevertheless, the somewhat consistent values of δ_{rel} obtained despite the heuristic character of both methods and the systematic limitations of the experimental setup are encouraging for further investigation. The method based on photo-diode voltage offers the greatest potential for improving reproducibility, and systematic refinement of this approach represents the next step in this line of research. To continue this line of research, the diode based method must be systematically developed to ensure repeatability of the experiments. A dedicated setup should aim to produce the desired spraying phenomenon for longer time periods to allow the measuring equipment to reach thermal equilibrium. These improvements to the presented method are also necessary for tests with refrigerant mixtures.

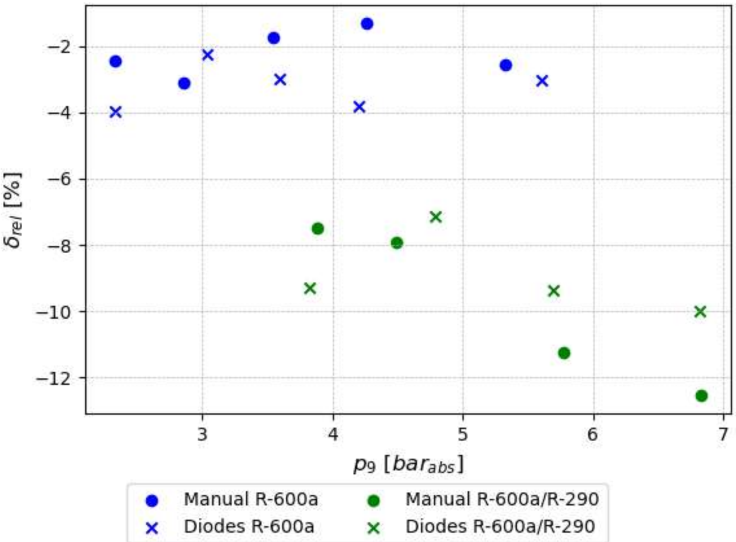

Figure 3: Relative deviation for manual observation of the sight glass and observation of U_{PD} for pure R-600a and for the R-600a/R-290 mixture

3.2. Fitting of Empirical Correlations to Approximate Vapor Pressure Curve

The coefficients of all four fitted empirical correlations, together with their valid temperature ranges based on the recorded data and the RMSE compared to the REFPROP vapor pressure within that range, are listed in Table 1. Figure 4a) and 4b) show the vapor pressure curves according to Equation (2) for pure R-600a and the R-600a/R-290 mixture, respectively. Figure 4c) and d) show δ_{rel} for the respective empirical correlations compared to the vapor pressure curve according to REFPROP. Since the underlying experimental data generally yields pressures below the vapor pressure at the corresponding temperatures, the fitted empirical correlations also underestimate the REFPROP curve. The empirical correlations for the mixture show larger deviations from the REFPROP saturation pressures, because of the larger differences in the measured data. The shape of δ_{rel} for the mixture empirical correlations also differs from that of the pure fluid, partly because the mixture datasets contain only four points instead of five: At a source temperature of 20 °C, spraying could not be produced reliably and is therefore excluded from this study. For pure R-600a, the best polynomial is less precise by a factor of 10 than measurements that are used for the development of reference equations of state (Miyamoto et al., 2004). Due to the heuristical nature of these tests, the source for misprediction can’t be precisely determined.

An important practical consideration is whether the empirical correlations for mixtures need to match the thermophysical vapor pressure curve precisely. For superheat control in heat pumps, the primary objectives are performance and compressor safety. Compressor safety requires the absence of liquid droplets in the suction line. For zeotropic mixtures, composition shifts during evaporation mean that liquid droplets can appear in the suction line before the thermophysical dew line of the expected composition is reached. In this context, a polynomial that accurately captures suction line superheat may be more relevant for control purposes than one that matches the thermophysical vapor pressure curve. If the diode-based method can be systematically developed to reliably identify this pseudo-dew line, the resulting empirical correlations are sufficient for superheat control applications. Alternatively, a control strategy based entirely on droplet detection, rather than on thermophysical property data, is

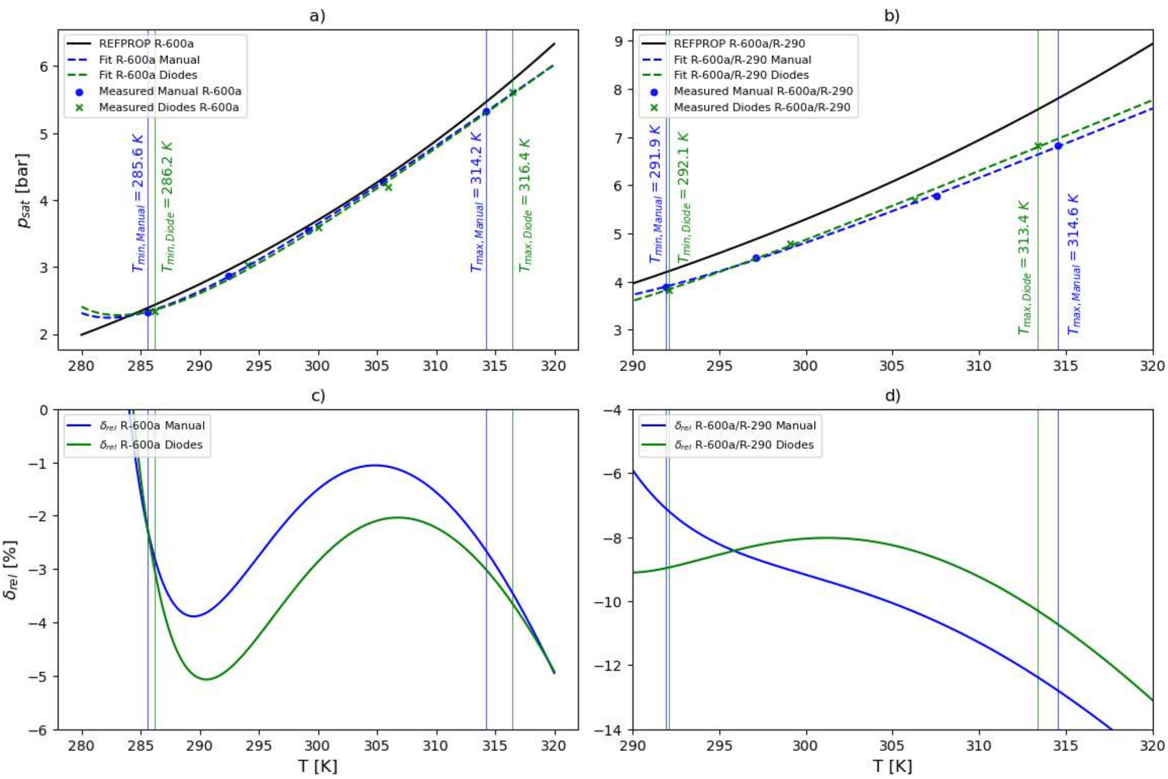

Figure 4: Vapor pressure curves for fitted empirical correlations for pure R-600a and R-600a/R-290 mixture and δ_{rel} for each empirical correlations; a) Vapor pressure curves for pure R-600a b) Vapor pressure curves for R-600a/R-290 mixture c) δ_{rel} for pure R-600a d) δ_{rel} for R-600a/R-290

Table 1: Temperature range, coefficients and RMSE of equation (2), regressed with data presented in Figure (3)

Data Set	T_{min} $[K]$	T_{max} $[K]$	c1	c2	c3	RMSE [kPa]
R-600a Manual	285.6	314.2	$1.4 * 10^1$	6	$-1.6 * 10^1$	12.3
R-600a Diode	286.2	316.4	$1.6 * 10^1$	6.5	-1.7	15.2
R-600a/R-290 Manual	291.9	314.6	$2.1 * 10^1$	7.9	-2.1	65.9
R-600a/R-290 Diode	292.1	313.4	$1.6 * 10^1$	6.9	-1.8	56.5

conceivable: if a small number of droplets is tolerated and a compact IHX is installed downstream of the evaporator, superheat control could be implemented without reliance on property data or fitted empirical correlations at all.

4. CONCLUSION

Two methods for the detection of trace amounts of liquid in a sight glass after the evaporator, either by manual observation or with a low cost diode based sensor, to approximate dew line temperatures are tested in a heat pump using pure R-600a and a mixture of R-600a with 40 %m R-290. Pressures are set by adjusting the source inlet temperature between 20 °C and 60 °C in 10 K steps for both methods and both fluids. For pure R-600a, the relative deviation of the saturation pressure from the REFPROP dew line remains below 6 %, and for the R-600a/R-290 mixture between 6 % and 14 %. For each dataset, the coefficients of the in-house empirical correlations are optimized to describe the dew line. The best fit for pure R-600a describes the dew line with an RMSE of 12.3 kPa (1.2 K), and for the mixture with an RMSE of 56.5 kPa (3.4 K). The reproducibility of the current methodology represents a major drawback of both approaches. The diode-based method holds the greatest potential for systematic further development. Finally, the practical purpose of the fitted empirical correlations warrants further discussion, as the thermophysical dew line of mixtures with large temperature glides may not serve as the most meaningful control target in heat pump systems, where liquid droplet formation in the suction line can precede the thermophysical dew line due to composition shifts during evaporation.

NOMENCLATURE

Abbreviations

IHX	Internal Heat Exchanger
LED	Light-Emitting Diode
P&ID	Piping and Instrumentation Diagram
PID	Proportional-integral-derivative (controller)
R-290	Propane
R-600a	Isobutane
RMSE	Root Mean Square Error

Variables

c_1, c_2, c_3	Coefficients of the empirical correlation	[-]
p	Pressure	[kPa]
Q	Vapor Quality	[-]
T	Temperature	[K]
ΔT	Temperature Difference	[K]
δ	Error	[-]

Subscripts

9	State Point 9
rel	Relative
sat	Saturation
sh	Superheat

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