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Reverse engineering of fluid selection for thermodynamic cycles with cubic equations of state, using a compression heat pump as example

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ABSTRACT

Fluid selection for thermodynamic cycles like refrigeration cycles, heat pumps or organic Rankine cycles remains an actual topic. Generally the search for a working fluid is based on experimental approaches or on a not very systematic trial and error approach, far from being elegant. An alternative method may be a theory based reverse engineering approach, proposed and investigated here: The design process should start with an optimal process and with (abstract) properties of the fluid needed to fit into this optimal process, best described by some general equation of state and the corresponding fluid-describing parameters. These should be analyzed and optimized with respect to the defined model process, which also has to be optimized simultaneously. From this information real fluids can be selected or even synthesized which have fluid defining properties in the optimum regime like critical temperature or ideal gas capacities of heat, allowing to find new working fluids, not considered so far. The number and kind of the fluid-defining parameters is mainly based on the choice of the used EOS (equation of state). The property model used in the present work is based on the cubic Peng–Robinson equation, chosen due to its moderate numerical expense, sufficient accuracy as well as a general availability of the fluid-defining parameters for many compounds.

The considered model-process works between the temperature levels of 273.15 and 333.15 K and can be used as heat pump for supplying buildings with heat, typically. The objective functions are the COP (coefficient of performance) and the VHC (volumetric heating capacity) as a function of critical pressure, critical temperature, acentric factor and two coefficients for the temperature-dependent isobaric ideal gas heat capacity. Also, the steam quality at the compressor entrance has to be regarded as a problem variable. The results give clear hints regarding optimal fluid parameters of the analyzed process and deepen the thermodynamic understanding of the process. Finally, for the COP optimization a strategy for screening large databases is explained. Several fluids from different substance groups like hydrogen iodide (COP = 3.68), formaldehyde (3.61) or cyclopropane (3.42) were found to have higher COPs than the often used R134a (3.12). These fluids will also have to fulfill further criteria, prior to their usage, but the method appears to be a good base for fluid selection.

1. Introduction

The selection of a working fluid is a crucial step in the design of heat pumps, refrigeration cycles and ORC (organic Rankine cycle)-processes. First of all, the fluid will influence the COP (coefficient of performance) or the thermal efficiency and also the specific size is influenced as e.g. measured by the VHC (volumetric heating capacity) of heat pumps. Besides those thermodynamic criteria the fluid selection e.g. also depends on environmental aspects like the toxicity or the flammability and on the current legislations. A recent overview of working fluid properties and selection criteria with respect to ORCs and Brayton cycles is provided by Gomez et al. [1]. In earlier times CFCs (chlorofluorocarbons) and HCFCs (hydrochlorofluorocarbons) were used as working fluids. Based on their high ODP (ozone depletion potential) those fluids were replaced by substances from the group of the HFCs (hydrofluorocarbons). HFCs do not have an ozone depletion potential but some of them however possess an extremely high GWP (global warming potential). Within the EU a law has already passed that prohibits the use of HFCs with a GWP above 150 for air conditioning systems in cars.

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Thus it is necessary to find new fluids in future that are more sustainable and lead to efficient processes.

Today, the usual thermodynamic approach of fluid selection and design includes the trial of several fluids for which thermodynamic data are available and calculating specific process parameters like the COP with some given boundary conditions and constraints (temperature and pressure levels etc.) as selection criteria for a defined process and finally the fluid which performs best is selected. For this standard approach, ample literature is available e.g.: [2–8]. This procedure, however, results in a high experimental or computational cost for every fluid to be tested and hence the possible number of tested fluids is clearly limited. Also, fluids for which the thermodynamic data are not well establishes are not considered. For the latter, a theoretically based approach of Brown et al. [9] tries to reduce the computational costs by using simply calculable equations of state like the cubic EOSs to predict the COPs. Furthermore, group contribution methods are applied to estimate the necessary fluid descriptive parameters like T_c, p_c, ω and c_p. Thus, also fluids for which only a few thermodynamic data are available can be considered. However, the strategy does not principally differ from the previously mentioned ones, since only known fluids are screened by this approach. Another problem of this approach is that the process is not adapted for each fluid. We will show that the optimizations of only one process parameter within a small domain for every considered real fluid leads to different rankings of the fluids. Thus, a combined fluid selection and process optimization is recommendable.

An alternative and possibly more effective approach is a reverse engineering approach for fluid selection with simultaneous process optimization. The main idea is to start with the given heat sources and heat sinks and the desired energy stream, either power or a heat flow at a certain temperature. The fluid properties are regarded as variables which can be selected and optimized for the given temperature levels to obtain an optimal cycle. Thus, after fixing further constraining values like maximum and minimum pressures or temperature differences at the pinch point, would be to establish a thermodynamic cycle with essential degrees of freedom and aiming to run with a high efficiency (somehow defined), with a minimum of exergy loss rate (or entropy production rate). The third step would be to define process variables like steam quality as well as fluid-descriptive parameters regarded as variables. The latter can either be defined on the macroscopic scale like critical point values combined with capacities of heat or parameters based on a molecular description of the macroscopic fluid properties, as used by the PC-SAFT EOS [10] can be chosen. After optimizing the process with these abstract variables a range of optimal parameter combinations will be found, generally not fitting to a real fluid. Thus, finally the approach would continue with the search of real fluids with parameters near to the optimal values. One of the possible advantages would be that fluids would be considered which would not be investigated in the standard approach. Also, critical values and gas phase capacities of heat are known for much more fluids than precise property relations, which are only known for a few dozen compounds so far. And even the synthesis of such molecules which come near to the desired values could be considered.

In practice, the procedure is not followed sequentially but is based on numerical optimization of typical fluid-descriptive parameters for a fixed process or with simultaneous process-optimization. By means of the results it is possible to screen also huge databases for some optimal fluids, easily. This method is dependent on an equation of state, which is preferably only based on a few fluid-descriptive parameters and reaches a reasonable accuracy.

Very recently, Lampe et al. did fluid-searching using a kind of reverse engineering method for ORC-processes [11,12] using the PC-SAFT EOS that depends on fluid-descriptive parameters at the molecular level. The authors call this optimization approach CAMD (computer-aided molecular design). The calculation of the PC-SAFT EOS is relatively complex and needs several fluid-parameters. Some other approaches follow the use of the BACKONE EOSs, which are highly accurate but also need comprehensive information about the fluid [13]. Another option, which is followed in the present work, would be the use of a cubic equation of state. Here, the needed fluid parameters are the critical temperature T_c, the critical pressure p_c and the acentric factor ω or alternatively the normal boiling point. This limited number of parameters is tabulated for many fluids. In addition, the temperature dependent isobaric heat capacities of the ideal gas are needed in order to determine all thermodynamic properties. Often it was assumed that the cubic EOS are not accurate enough to describe the performance of fluids as refrigerants [13]. Brown et al. [9,14]. analyzed among others the deviation of the COP and the VCC (volumetric cooling capacity) using the Peng–Robinson EOS [15] combined with a model for the ideal gas heat capacity from REFPROP [16] for 26 refrigerants in total; in his highest accuracy scenario, he showed, that the absolute mean error amounts to about 1.34% only and the maximum deviation was 7.2%. Related to the first step of fluid selection this accuracy can be accepted as good enough, considering that also fluids may be discovered as possible refrigerants, which were not even considered before.

The fluid property model used in the present work is also based on the Peng–Robinson EOS and uses a 5 parameter equation to evaluate the isobaric heat capacity of the ideal gas and thus to calculate enthalpies and entropies for the different states of the process. For the optimization, a linear temperature dependence of the isobaric ideal gas heat capacities is used. The analysis and the optimization of the process with respect to the mentioned process variables also helps to get a systematic understanding of the importance of different fluid parameters, which appears to be more satisfying than a mere list of names of better and not as good working fluids.

The reverse engineering method shall be investigated in the present paper, and, thus, a model process had to be chosen for evaluation. As an example the fluid selection for a simple vapor-compression heat pump process is selected. Based on a heat pump system for heating buildings the considered process works between the temperature levels of 273.15 K in the evaporator and 333.15 K in the condenser. Recently, heat pump systems are finding broader use for heating buildings; especially ground source heat pumps have a good COP and are a means for saving resources and decreasing CO_2 emissions. Today's working fluids of heat pumps are usually also HFCs or HCFCs like R-134a, R-32, R-125 or mixtures of them and have to be replaced in future. The fluid and process

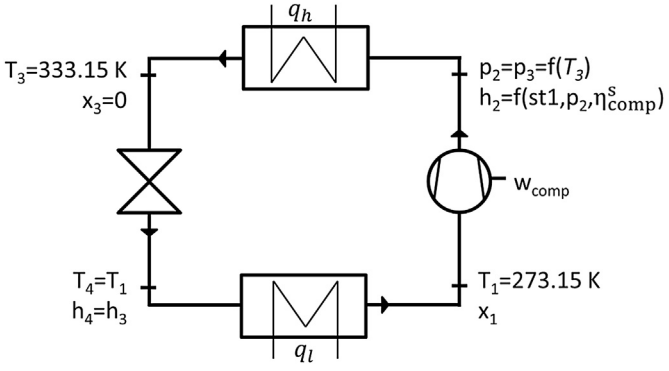

Fig. 1. Working principle of the investigated heat pump cycle.