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How to predict the vapor slope of temperature-entropy saturation boundary of working fluids from molecular groups?

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ABSTRACT

The vapor slope of temperature-entropy saturation boundary of working fluids has a significant effect on the efficiency and the safety of thermodynamic processes. Therefore, how to predict the vapor slope efficiently and quickly is worth studying. In this work, the vapor slope represented by the slope angle is firstly correlated with the reduced temperature, the molecular weight, 10 molecular groups and a topological index. The 10 molecular groups can cover most working fluids employed in thermodynamic cycles. The chosen topological index is able to distinguish all the isomers of working fluids. The relationship between the slope angle and these variables is established by an artificial neural network. A total of 4338 data points for 54 working fluids are used to create this network. These data are calculated from the highly accurate Helmholtz energy equation at the reduced temperature range of 0.6–1. The predicted results from molecular groups show a good agreement with desired slope angles. The average absolute deviations for training, validation and test sets are 0.68%, 0.64%, 0.68%, respectively. In the selection and design of working fluids, the established model can be easily employed to predict the saturated vapor slope only from the molecular structures.

1. Introduction

Thermodynamic cycles, such as refrigeration, heat pump, and organic Ranking cycle, have been comprehensively applied in cooling, heating and power generation. These cycles generally employ working fluids to transfer heat and generate work. The thermodynamic processes of working fluids are usually presented on the temperature-entropy (T-s) diagram for the visualization, design and analysis of the cycle. Furthermore, in order to reveal the change of working fluid phase state for every thermodynamic process, the temperature-entropy saturation boundary of working fluid is also displayed on the T-s diagram. In fact, the geometry of temperature-entropy saturation boundary of working fluid has a significant effect on the thermodynamic performance of cycle processes. Based on the phase boundary of working fluids, many published papers have conducted the selection of working fluids [1], the design and optimization of thermodynamic cycles [2,3].

As stated by Liu et al. [4], working fluids can be classified into dry fluids with positive slopes, wet fluids with negative slopes, and isentropic fluids with infinite slopes, according to the geometry of saturation vapor curve. The sign of the saturated vapor slope has a great impact on the performance of expansion or compression process, and directly determines the safety of expander or compressor. For the expansion process of power cycle, the working fluids with isentropic or dry behaviors are commonly required [4,5]. The reason is that the expansion of wet working fluids may induce condensation of saturated vapor and make fluids enter into the region of two-phase at the outlet of expander. However, for the vapor compression reverse cycle, the working fluids with wet or isentropic behaviors are preferred to avoid the formation of the liquid droplets in the compressor [6]. Furthermore, in the selection of working fluids and the optimization of thermodynamic cycles, the isentropic point where the tangent line of the saturated vapor curve is vertical, is usually applied to determine the maximum cycle temperature [7].

Considering the significant effect that the saturated vapor slope has on the thermodynamic performance of the working fluids, a number of models have been developed to describe the geometry of saturation vapor curve for working fluids. For instance, Morrison [6] reported simplified relationships to estimate the saturated vapor slope over low to moderate pressure ranges. He concluded that the shape differences of the phase boundary among working fluids

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Nomenclature

Symbols

a	Molar Helmholtz energy, J/mol
AAD	Average absolute deviation
ANN	Artificial neural network
bias	Average percent deviation
BP	Back propagation
CAMD	Computer aided molecular design
EATII	Topological index
GCM	Group contribution method
LM	Levenberg-Marquardt
M	Molecular weight, g/mol
MSE	Mean square error
N	Number of data points
P	Pressure, Pa
RMS	Root mean square error
s	Entropy, J/(mol·K)
T	Temperature, K
v	Molar volume, m^3/mol

Greeks

θ	Slope angle, °

Subscripts

c	Critical temperature
prediction	Predicted value of slope angle
target	Desired value of slope angle

are caused by molecular structures. Liu et al. [4] developed another simplified relationship to predict the slope of saturated vapor, based on the relationship between the enthalpy of evaporation and the temperature. However, the established model is only limited to the low-pressure range. In their analysis, Liu et al. confirmed that the presence of hydrogen bonds may result into wet behavior due to a large evaporation enthalpy. Garrdo et al. [8] obtained analytical expressions for predicting the slope and curvature of the temperature-entropy saturation boundary of working fluids on the basis of Helmholtz energy and typical equations of state. The classification of fluids in wet, isentropic or dry behavior was deduced to a simple criterion based on a dimensionless function. Furthermore, the authors [9] employed the highly accurate Helmholtz energy equation to get the rigorous analytical expression on the slope of saturated curve for pure and mixed working fluids. The effect of molecular groups and mixture compositions on the saturated slope was revealed. However, it should be noted that the application of the above proposed models generally requires physical constants of working fluids, and the parameters of Helmholtz energy equation are obtained from the experimental data fitting of thermodynamic properties. Therefore, for the novel working fluids, which are generated by the combination of molecular groups via computer-aided molecular design (CAMD) [10,11], the existing models are inappropriate to predict the saturated vapor slope. In order to describe the geometry of saturation vapor curve for any working fluid, a group contribution method (GCM) is proposed to predict the saturated slope in this work. Furthermore, considering the large number of isomers existing in working fluids, a topological index is introduced to distinguish the structural isomers.

As for the establishment of the complex relationship between the molecular structures and the saturated vapor slope of working fluids, artificial neural network (ANN) is a suitable alternative. Compared with the classical methods, the advantages of ANN are speed, simplicity and capacity to learn from experiments. ANN can simulate the nonlinear relationship between structural information and properties of working fluids during the training process and then generalize the knowledge among homologous series without the need for theoretical formulas [12]. In fact, a vast number of artificial neural network-group contribution methods (ANN-GCMs) have been proposed to predict various properties of working fluids. For example, Moosavi et al. [13,14] used an ANN-GCM to predict liquid density of refrigerant systems. Farhad et al. [15] employed an ANN-GCM to determine the critical properties and acentric factor of working fluids. Based on the particle swarm algorithm, an ANN-GCM was proposed by Juan [16] to estimate the freezing temperature of working fluids. Furthermore, the authors [17] developed an ANN to predict the boiling temperature of working fluids from molecular groups and a topological index. From the results of the above published papers, it can be concluded that the ANN-GCM model is highly accurate in predicting the properties of working fluids.

The purpose of this study is to employ an ANN to establish the relationship between the molecular structures and the saturated vapor slope of working fluids, so that the established ANN-GCM can predict the vapor slope of phase boundary for working fluids only from the molecular structures. The model input consists of the reduced temperature, the molecular weight, 10 molecular groups and a topological index. The vapor slope expressed by the slope angle is defined as the model output. The detailed ANN-GCM modeling for the prediction of saturated vapor slope is demonstrated in Section 2. In Section 3, the performance of the established network is analyzed and discussed. A summary of the developed model is presented in Section 4.

2. ANN-GCM modeling

The ANN-GCM model can predict the properties of working fluids from the molecular groups via ANN. In general, ANN consists of a number of neurons working in unity to solve various scientific and engineering problems. A feed forward back propagation (BP) neural network is employed to predict the saturated vapor slope in this work. The BP neural network is based on the error back propagation, and it has been confirmed that a three layer's BP network can approximate any rational function with arbitrary precision [18]. Therefore, in this study, the employed BP network consists of an input layer, an output layer and a hidden layer. In order to predict the saturated vapor slope from the molecular structures of working fluids accurately, the model details of BP network, such as the network parameters and the data set, are presented in the following subsections.

2.1. Input parameters

For the ANN-GCM model, molecular groups should be considered as the input parameters of BP network. The value associated with each group is defined as: 0 when the group does not appear in the working fluid and x when the group appears x times in the substance. Furthermore, a large number of group division methods for organic compounds have been demonstrated in the published