# New knowledge on the temperature-entropy saturation boundary slope of working fluids

Wen Su, Li Zhao[*], Shuai Deng

*Key Laboratory of Efficient Utilization of Low and Medium Grade Energy, Tianjin University, MOE, Tianjin, 300072, China*

## ABSTRACT

The slope of temperature-entropy saturation boundary of working fluids has a significant effect on the thermodynamic performance of cycle processes. However, for the working fluids used in cycles, few studies have been conducted to analyze the saturated slope from the molecular structure and mixture composition. Thus, in this contribution, an analytical expression on the slope of saturated curve is obtained based on the highly accurate Helmholtz energy equation. 14 pure working fluids and three typical binary mixtures are employed to analyze the influence of molecular groups and mixture compositions on the saturated slope, according to the correlated parameters of Helmholtz energy equation. Based on the calculated results, a preliminary trend is demonstrated that with an increase of the number of molecular groups, the positive liquid slope of pure fluids increases and the vapor slope appears positive sign in a narrow temperature range. Particularly, for the binary mixtures, the liquid slope is generally located between the corresponding pure fluids', while the vapor slope can be infinity by mixing dry and wet fluids ingeniously. It can be proved through the analysis of mixtures' saturated slope that three types of vapor slope could be obtained by regulating the mixture composition.

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## 1. Introduction

In the energy conversion, thermodynamic cycles play a significant role. So far, the typical technologies of development and utilization of low grade heat consist of power cycle represented by Organic Rankin Cycle (ORC) and vapor compression reverse cycle represented by refrigeration/heating cycle. ORC can convert the low and medium temperature heat into mechanical or electrical power efficiently, and Vapor compression reverse cycle can realize the heat transfer from the low temperature to high temperature environment. However, no matter the thermodynamic cycle is positive or negative, it employs working fluids to generate work or transfer heat. As the properties of working fluids directly determine the thermodynamic efficiency of system, the design of system components, the stability and safety of system, many published literature have focused on the selection and design of pure working fluids for various thermodynamic cycles [1,2]. Furthermore, in order to improve the cycle efficiency and the operation flexibility, mixtures, whose individual drawbacks of the components can be compensated by each other, are recommended as candidates of working fluids [3].

For conventional thermodynamic cycles, the thermodynamic processes can be presented on the temperature-entropy (T-s) diagram for the visualization, design and analysis of the cycle. An example for the important role of T-s in thermodynamic analysis is presented in Fig. 1, based on the active research field on ORC. The area surrounded by all processes represents the net output power of the cycle per kilogram of working fluid, and an opening downward curve denotes the phase boundary of working fluid. The left side of the curve is the liquid branch of phase boundary, while the vapor branch lies in the right side of the curve. It can be found that the slope of the phase boundary mainly influences the compression and expansion processes of working fluids, which are realized through pump and expander in the cycle. Furthermore, the phase diagram presented in Fig. 2 indicates that each working fluid has different slopes of phase boundary. The phase boundaries of various working fluids directly lead to the diversity of surrounded area of a specific cycle. Therefore, the cycle performance strongly depends on the relationship between the loop path of the cycle and the edge of working fluid's phase boundary.

For the pure working fluids, the slope of saturated liquid is positive. In the power cycle, the liquid phase boundary significantly

* Corresponding author. Tel.: +86 022 27404188.
E-mail address: jons@tju.edu.cn (L. Zhao).

**Nomenclature**

*Symbols*
| | |
|---|---|
| $a$ | Molar Helmholtz energy J/mol |
| $c$ | Heat capacity J/(mol·K) |
| EOSs | Equations of state |
| $M$ | Molar mass g/mol |
| ORC | Organic Rankine cycle |
| $P$ | Pressure Pa |
| $s$ | Entropy J/(mol·K) |
| $T$ | Temperature K |
| $u$ | Internal energy J/mol |
| $v$ | Molar volume m³/mol |

*Greeks*
| | |
|---|---|
| $\beta_s$ | Visible slope kg·K²/kJ |

*Subscripts*
| | |
|---|---|
| $b$ | Normal temperature; |
| $c$ | Critical temperature |
| eq | Equilibrium |
| $r$ | Reduced temperature |
| $v$ | Isochoric |
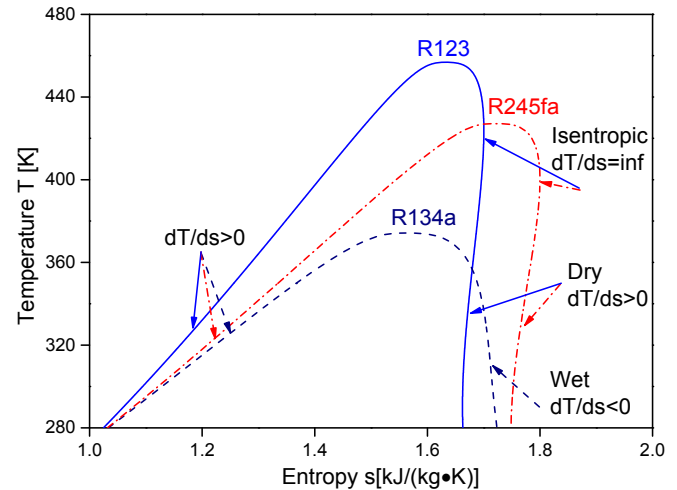


**Fig. 2.** Temperature-entropy saturation boundary for different working fluids.



**Fig. 1.** A case of thermodynamic cycle in temperature-entropy diagram.

influences the compression process of working fluids [4]. When the saturated liquid curve is near to the vertical, the working fluids at the outlet of the pump might be at a saturated liquid state or two-phase state theoretically. This characteristic of working fluids will pose a great challenge to the engineering design of pump. For the expansion process of power cycle, the working fluids with isentropic or dry behaviors are commonly required [5,6]. 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. Furthermore, in the selection of working fluids, the point of the vapor saturated line where the tangent line is vertical is also employed to determine the maximum temperature of dry working fluids at the inlet of expander [7]. On the contrary, for the vapor compression reverse cycle, the working

fluids with wet or isentropic behaviors are more preferred to avoid forming the liquid droplets in the compressor. Although the working fluids' phase boundary slope has a significant influence on the thermodynamic processes, few literature have been published to study the effect of molecular structures on the phase boundary slope for the selection and design of appropriate working fluids.

For the mixed working fluid, composition has a significant effect on the slope of phase boundary. In the recently proposed cycles, such as the heat pump using vapor expander to recover the expansion work [8], the mixed working fluids, which consist of wet and dry fluids, are employed to realize the compression and expansion processes. In order to avoid the formation of liquid droplets, a composition regulator is used to get the desired slope for the corresponding processes. In fact, for the cycles involved the compression and expansion processes, the working fluids with isentropic behavior can satisfy the required characteristics of temperature-entropy simultaneously. However, the general relationship between the composition and the phase boundary slope has not been established. The influence of the mixture composition on the slope is required to be further investigated.

In fact, owing to the significant effect of the saturated slope on the thermodynamic processes, a number of models have been proposed to predict the saturated slope of working fluids. Morrison [9] developed simplified relationships of varying accuracy to estimate the saturated vapor slope over low to moderate pressure ranges. He concluded that the differences, which mean the shape of the phase boundary, varies dramatically from one fluid to another, are caused by molecular structures. Another simplified relationship for predicting the slope of saturated vapor was obtained from the relationship between the enthalpy of vaporization and temperature by Liu et al. [5]. In their analysis, Liu et al. confirmed that the presence of hydrogen bonds may result into wet behavior due to a larger evaporation enthalpy. Then, Garrdo et al. [10] obtained analytical expressions for predicting the slope and curvature of the temperature-entropy saturation boundary of pure fluids using Helmholtz energy and typical equations of state (EOSs). The classification of fluids in wet, isentropic or dry behavior was deduced to a simple criterion based on a dimensionless function. It should be noted that the above models developed to describe the phase behaviors of working fluids are not derived from the rigorous thermodynamic relationships. In addition, these models focus on the vapor slope of pure fluids. 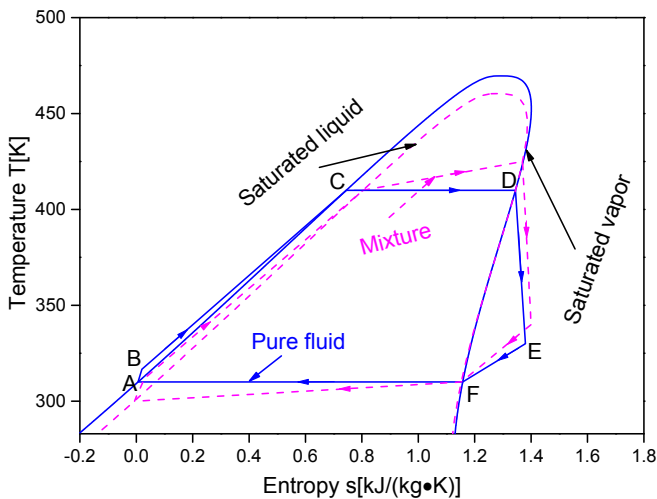So far, few works about the saturated