



Characterizing wet and dry fluids in temperature-entropy diagrams

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ABSTRACT

In this work we show that the shape of the liquid-vapor saturation curve in a T_r-s^* diagram ($T_r = T/T_c$ and $s^* = s/R$, with T_c the critical temperature, s the molar entropy and R the gas constant) for a given fluid is mainly governed by the acentric factor, ω , and the critical molar volume, v_c , of the fluid. The study uses as reference the point M where the saturated vapor curve in the T_r-s^* diagram changes its concavity, i.e. $(d^2s^*/dT_r^2)_M = 0$. By analyzing the data provided by the National Standards and Technology (NIST) program RefProp 9.1 for 121 fluids, we find that, at this point, $T_{Mr} \approx 0.81$ and the slope $\xi_M^* = (ds^*/dT_r)_M$ is well correlated with v_c , existing a threshold value $v_{c,0} \approx 0.22 \text{ m}^3 \text{ kmol}^{-1}$ so that $\xi_M^* < 0$ (wet fluid) for $v_c < v_{c,0}$ and $\xi_M^* > 0$ (dry fluid) for $v_c > v_{c,0}$. This direct relation between v_c and the wet or dry character of a fluid is the main result of the present work. Furthermore, the dimensionless vaporization entropy at the reference point M, $\Delta_v s_M^* = s_M^{*g} - s_M^{*l}$, increases in a nearly linear way with ω .

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1. Introduction

Thermodynamic liquid-vapor saturation properties of working fluids affect efficiency, utility costs, maintenance and environmental impact of engineering systems such as vapor-compression based refrigeration, heat pump devices and Rankine cycles. In particular, the choice of working fluids is very important in organic Rankine cycles (ORC) [1]. An ORC works like a conventional Rankine cycle but uses an organic working fluid instead of water and it has been designed for producing electrical power from renewable energies (wind, solar, geothermal, biomass) or from low-temperature waste heat.

A crucial aspect for the selection of a working fluid in an ORC is its saturation liquid-vapor curve in a temperature-molar entropy ($T-s$) diagram. Depending on the slope, dT/ds^g , of the saturated vapor branch, three types of fluids are considered: dry fluids with positive slopes, wet fluids with negative slopes, and isentropic fluids with nearly infinite slopes. Dry and isentropic organic fluids are usually used in ORC's because they do not present condensation after isentropic expansion in the turbine.

In 2004, Liu et al. [2] proposed to consider the inverse of the slope of the saturated vapor curve, $\xi = ds^g/dT$, on the $T-s$ diagram

in order to classify the fluids. After some simplifications, these authors derived for ξ the following temperature dependent expression

$$\xi = \frac{c_p^g}{T} - \frac{1 - (1-n)T_r}{1 - T_r} \frac{\Delta_v h}{T^2}, \quad (1)$$

where c_p^g is the isobaric molar heat capacity of the saturated vapor, $T_r = T/T_c$ the reduced temperature, being T_c the critical temperature, $\Delta_v h$ is the molar enthalpy of vaporization, and $n \approx 0.38$ is the exponent appearing in the well-known Watson relation for the temperature dependence of $\Delta_v h$ [3,4]. Finally, Liu et al. [2] computed the value of ξ at the normal boiling temperature, T_b , of the fluid in order to predict its behavior in the turbine expansion process: $\xi_b \equiv \xi(T_b) < 0$, wet fluid; $\xi_b \sim 0$, isentropic fluid; and $\xi_b > 0$, dry fluid. In 2007, Invernizzi et al. [5] introduced a *parameter of molecular complexity* which is equal to ξ expressed in reduced units and evaluated at a reduced temperature $T_r = 0.7$, and proposed an approximate expression, different from (1), to evaluate this parameter.

Chen et al. [6] showed that large deviations can occur when using equation (1) to compute ξ at off-normal boiling temperatures. These authors recommended to use the temperature and entropy data, if they are available, to directly calculate ξ at the required temperature. Since 320 K is the approximate design temperature for condensation in an ORC, these authors calculated ξ at this

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Nomenclature		Superscripts	
$\Delta_v h$	Molar enthalpy of vaporization, J/mol	*	Dimensionless
ν	Molar volume, m ³ /kmol	g	Saturated vapor
σ_c	Intermolecular separation at zero potential energy, nm	l	Saturated liquid
c_p	Isobaric molar heat capacity, J/(mol K)	<i>Subscripts</i>	
c_{sat}	Molar heat capacity along the saturation line, J/(mol K)	0	Reference value that separates wet fluids from dry fluids
N_A	Intermolecular separation at zero potential energy, nm	1,2	Points for which $\xi^* = 0$
p	Pressure, MPa	b	Normal boiling
R	Gas constant, 8.314472 J/(mol K)	c	Critical
s	Molar entropy, J/(mol K)	M	Point for which $\xi^*(T_r)$ presents a maximum
T	Temperature, K	r	Reduced
		tp	Triple point
		v	Vaporization
<i>Greek letters</i>		<i>Acronyms</i>	
ω	acentric factor	CSP	Corresponding states principle
ξ	Inverse of the slope of the saturated vapor curve, J/(mol K ²)	NIST	National Institute of Standards and Technology
		ORC	Organic Rankine cycle

temperature for fluids with $T_c > 320$ K, and at 290 K by assuming that for $T_c < 320$ K the condensation is designed to be at 290 K. Hærvig et al. [7] evaluated ξ at the temperature for which $d^2s^g/dT^2 = 0$ for dry fluids and at 293 K for wet fluids corresponding to approximately the condensing temperature. If the temperature at which $d^2s^g/dT^2 = 0$ does not occur between 293 K and T_c , then ξ was calculated at 293 K for dry fluids as well.

This work presents a thermodynamic study of the liquid-vapor saturation curve in a T_r-s^* diagram, where T_r is the reduced temperature and $s^* = s/R$, being R the gas constant. Our aim is to compare this saturation curve for different fluids in the scheme of the corresponding states principle (CSP) in order to analyze the possibility of characterizing the shape of the curve in terms of a reduced number of well-known parameters of the fluid. In this context, we note that the use of the dimensionless molar entropy s^* instead of s allows for obtaining dimensionless results in a CSP scheme without any loss of generality. The analysis is made from temperature and entropy liquid-vapor saturation data of the 121 fluids considered by the National Institute of Standards and Technology (NIST) program RefProp 9.1 [8].

The main objectives of this paper are: (i) Analyze the wet or dry character of working fluids in ORC cycles according to a CSP scheme. (ii) Identify the key parameters that determine the shape of the liquid-vapor saturation curve in a temperature-entropy representation. (iii) Analyze the different relations that arise between these parameters and other characteristic parameters of the fluids.

This work is structured as follows. In Section 2 we analyze the main features of the liquid-vapor saturation curve in a T_r-s^* diagram and introduce the relevant parameters in the problem like the reduced temperature T_{Mr} where the inverse of the slope of the vapor saturated branch of the T_r-s^* diagram reaches a maximum value ξ_M^* . In Section 3 we present and discuss the results for the fluids considered in our study. We conclude with a brief Summary.

2. Theory

The liquid-vapor saturation curve in a T_r-s^* diagram presents a more or less inclined forward bell or dome shape with two branches, for all fluids considered in the RefProp 9.1 program [8]. The liquid saturated branch always presents a positive slope while

there are two possibilities for the slope of the vapor saturated branch: either it is negative for any temperature between the triple and the critical point or it can present a zone with positive values. Furthermore, in all studied fluids, the inverse of the slope of the vapor saturated branch attains a maximum value $\xi_M^* \equiv (ds^g/dT_r)_{T_{Mr}}$ at a point M with reduced temperature $T_{Mr} \approx 0.81$. The physical meaning of the maximum M becomes clear by noticing that those fluids with $\xi_M^* < 0$ always have a negative slope for the vapor saturated branch and, consequently, they are wet fluids. Obviously, those fluids with $\xi_M^* > 0$ present a zone around the maximum M with positive slope for the vapor saturated branch, behaving as dry fluids.

The significance of the point M in a T_r-s^* diagram is that at M this curve changes from concave to convex, i.e., $(d^2s^g/dT_r^2)_{T_{Mr}} = 0$. This suggests to take this inflection point as a reference in order to characterize the shape of the liquid-vapor saturation curve in a T_r-s^* diagram. In particular, one can take the dimensionless vaporization entropy $\Delta_v s_M^* = s_M^{*g} - s_M^{*l}$ as a measure of the ‘width’ of the curve, and the inverse of the slope $\xi_M^* = (ds^g/dT_r)_{T_{Mr}}$ as a measure of the ‘inclination’ of the curve. As mentioned above, we call ‘wet’ fluids those for which $\xi_M^* < 0$ and ‘dry’ fluids those for which $\xi_M^* > 0$. Obviously, fluids are either wet or dry but those with $|\xi_M^*|$ close to zero can be termed as isentropic. In the case of dry fluids there are two points at reduced temperatures T_{1r} and T_{2r} , ($T_{1r} < T_{Mr} < T_{2r}$), at which $\xi_1^* = \xi_2^* = 0$, being $\xi^*(T_r)$ positive for any value of T_r in the range (T_{1r}, T_{2r}) , and negative out of this range. In the next Section we analyze T_{Mr} , T_{1r} , T_{2r} , ξ_M^* and $\Delta_v s_M^*$ in terms of the acentric factor, ω , and the critical parameters, (T_c, p_c, v_c) , being p_c the critical pressure and v_c the critical molar volume, of the considered fluids. Besides its intrinsic thermodynamic interest, this analysis provides a set of semi-empirical guidelines which can help in the election of the working fluid in an ORC for a given operation design.

3. Results and discussion

3.1. Wet and dry fluids

Fig. 1 shows the liquid-vapor saturation curve in a T_r-s^* diagram for xenon and pentane. These curves are plotted from temperature

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