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A rigorous and accurate approach for predicting the *wet-to-dry* transition for working mixtures in organic Rankine cycles

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Abstract

Working fluids play a relevant role in solvent screening, which is required to analyze the performance of cool and power generation. In this contribution, a solidly thermodynamic-based criteria has been developed in order to provide a rational guide, capable of qualitatively and quantitatively predicting the effects of adding solvents. The latter with the aim of modify the performance of a given fluid by the addition of key agents, thus seeking to induce or inhibit some desirable or undesirable properties. This development is rigorous and applicable directly to any model through systematic applications of Legendre transforms. Both, slope and curvature of the temperature vs. entropy boundary have been analytically developed and applied to binary mixtures. Moreover, a dimensionless function which depends only on configurational properties is presented. Foremost, this theoretical framework was applied to van der Waals fluids due to their qualitative accuracy. For this approach, the behavior of simple and azeotropic mixtures is shown and an untold phenomenon constituted by multiple isentropic transitions for a single mixture has also been described. For quantitative descriptions, PC-SAFT EoS has been selected in its simplest form in order to render the behavior of mixtures composed by linear hydrocarbons and fluorocarbons.

Keywords: Organic Rankine cycle (ORC); Working mixtures; Low-grade heat; *T-S* diagram; Fluorocarbons; SAFT

1. Introduction

Conventional power cycles require significant amount of energy for their operation and in the most cases they are not capable of taking advantage of low-grade heat from alternative sources. In contrast, organic Rankine cycles (ORC) are an interesting technology and also essential as an environmental suitable alternative to conventional cycles. The main factor for this affirmation is the imperative necessity of more efficient technologies of power and cool generation. The latter, using waste heat of variable temperature from other processes and sources [1], like solar, geothermal, biomass or ocean energy sources, which are normally low-grade heat in contrast with other thermal sources like fossil fuels or nuclear power.

The working fluids are usually classified as *wet*, *dry* or *isentropic*, this depending on the slope of the dewline in the temperature *vs.* entropy projection. Fig. 1 shows a schematic representation of the transition between a *wet* to a *dry fluid* through an *isentropic* behavior of the dew-line. The aforementioned taxonomy

is in direct relation with an adiabatic and isentropic expansion from a superheated vapor [2]. In the case of a wet fluid, an expansion of the cited characteristic leads, in the most common of the events, to a partial condensation of the fluid, as can be seen in Fig. 1a. In 1a, a superheated fluid at the point (A) is expanded until point (B). Conversely, if a dry fluid is isentropically expanded from a superheated state (A), the final condition at the point (B) is always a superheated vapor, as in the system displayed in Fig. 1c. As expected, the limiting case is an isentropic system shown in Fig. 1b. In this case the expansion will close as a superheated vapor. Despite this, an isentropic system may behave as a wet compound at low temperature. It is expected that a dry fluid has better performance as a working fluid in ORCs compared with a working fluid which exhibits a wet behavior [3]. This is because a dry fluid remains as a superheated vapor after an isentropic expansion, where the useful work is produced. Thus, the risks of damage such as surface erosion by liquid impingement [4] and overheating the vapor at the boiler for preventing condensation over turbomachinery [5, 6] are avoided in the turbine blades.

From a practical perspective, the wet behavior has

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