



Methodology for estimating thermodynamic parameters and performance of working fluids for organic Rankine cycles



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ABSTRACT

In this paper, a simple methodology of applying the Peng–Robinson (P–R) EoS (Equation of State) to easily, quickly, and inexpensively evaluate and screen the performance potentials of many thousands of working fluids in ORC (organic Rankine cycles) is presented. The P–R EoS can be applied both to well-described (considerable experimental data is available) and not-so-well-described (little or no experimental data is available) working fluids. For not-so-well-described working fluids the P–R EoS can be constructed from thermodynamic parameter estimates using simple group contribution methods. In particular, they can be used to estimate the critical state properties, ideal gas specific heat at constant pressure, and acentric factor from knowing only a working fluid's molecular structure and its NBP (normal boiling point) temperature. The simulations presented in this paper represent a large variety and number of working fluids for several different ORC applications and operating conditions. The simulations using the P–R EoS based on knowing only a working fluid's molecular structure and its NBP temperature showed comparable accuracies to simulations based on using much more complex EoS based on large amounts of experimental data.

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1. Introduction

The world consumes an enormous amount of energy. One could argue that modern, developed economies are driven by energy and that the well-being (e.g., access to adequate nutrition, health services, and peaceful coexistence) of populations in developing and underdeveloped economies are, in part, tied to the availability of and access to adequate energy resources. Furthermore, for the benefit of humanity and the world at large, energy must be used in a way that minimizes the negative impacts on the environment, ecosystems, and climate, and moreover, must be used in such a way as to ensure adequate resources for future generations, that is, energy should be used in a sustainable manner.

In order to provide a sense of the enormity of the “problem of energy” and to place the current paper in context, consider that in 2010 the world consumed 5.53×10^{20} J of primary energy [1] and is projected to consume 8.65×10^{20} J by 2040 [1], an average annual increase of 1.5%. Electricity is one of the most widely consumed forms of energy by end users and accounts for a large portion of the primary energy consumed for all purposes. In fact in 2010, the world generated 0.73×10^{20} J of electricity [1] and is projected to

generate 1.40×10^{20} J by 2040 [1], an average annual increase of 2.2%. Assuming a constant average thermal conversion efficiency of 38% [1], electricity generation accounts for 34.6% of the world's total primary energy consumption in 2010 [1] and is projected to grow to account for 42.6% in 2040 [1].

Hydrocarbon fuels account for the majority of the primary energy consumed to produce electricity. For example in 2010, hydrocarbon fuels accounted for 66.6% of the worldwide electricity generation [1], while renewables—other than hydroelectric—accounted for only 3.8% of the total [1]. Despite the small contribution of renewables, they are projected to represent 8.6% of the total by 2040 [1], increasing by over 225% in the next thirty year period.

Regardless of the primary energy source, the overwhelming majority of electricity production is accomplished through the conversion of thermal energy into mechanical work in what can generically be termed a “heat engine,” with the maximum thermal efficiency being that of the Carnot cycle, where the Rankine cycle is the practical cycle most widely implemented to “mimic” the Carnot cycle.

The combustion of hydrocarbon fuels generally produces a high-temperature thermal energy source making water an “ideal” working fluid in these applications. However, as the source temperature drops, as is the case for many renewable/waste energy

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Nomenclature

c_p^0	ideal gas specific heat at constant pressure [kJ/kg K]
h	enthalpy [kJ/kg]
h_{fg}	latent heat of vaporization [kJ/kg]
\dot{m}	mass flow rate [kg/s]
M	molar mass [kg/kmol]
P	pressure (kPa)
T	temperature ($^{\circ}\text{C}$, K)
T^*	non-dimensional temperature, $T^* = T_r = T/T_c$
s	entropy (kJ/kg K)
s^*	non-dimensional entropy = $(s - s_{f,T_r=0.7})/s_{fg,T_r=0.7}$
v	specific volume [m^3/kg]
x	quality
Z	compressibility factor

Greek symbols

η_p	pump isentropic efficiency [%]
η_t	turbine isentropic efficiency [%]
η	cycle thermal efficiency [%]
Π	integral of ζ over the temperature range $0.6 < Tr < 0.9$, = $\int_{0.6Tr}^{0.9Tr} \zeta \cdot dT$, see Eq. (3)
ρ	density [kg/m^3]
ω	acentric factor
ζ	any thermodynamic property

Subscripts

c	critical
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est	estimated
f	saturated liquid
g	saturated vapor
high	high-side
–IHX	without internal heat exchanger
+IHX	with internal heat exchanger
low	low-side
max	maximum
out	outlet
p	pump
r	reduced
ref	reference
sat	saturation
t	turbine
vap	vapor

Acronyms

EoS	Equation of State
E%	percent error, see Eq. (2)
FEQ	fundamental Helmholtz equation
IHX	internal heat exchanger
NBP	normal boiling point
ORC	organic Rankine cycle
P–R	Peng–Robinson
R–K	Redlich–Kwong
RMSE%	root mean square percent error, see Eq. (1)

sources, water becomes a less attractive working fluid. In these cases, there is a strong need to identify additional and more appropriate working fluids for these applications. In fact, the systems used for these purposes are often dubbed ORC (organic Rankine cycles) to indicate the working fluid is typically an organic compound that is more appropriate (“ideal”) than water for these lower source temperatures.

If the goal for more widespread use of ORC systems could be realized, it would likely lead to increases in the amount of electricity generation from renewable/waste energy sources. Widespread use of ORC, however, is inhibited by the limited availability of working fluids appropriate for these lower (relative to the combustion of hydrocarbon fuels) source temperatures. The public domain literature contains several studies which have attempted to identify appropriate working fluids. The current paper does not claim or intend to present a detailed literature review of these papers. Instead the current paper limits its comments to two recent papers [2,3] that focused on working fluids appropriate for “low temperature” [2] and “high temperature” [3] applications. While these two papers (from the same research group) do not exhaust all potential working fluids, they do discuss a relatively large number (42) of single-component working fluids.

We focus on these two papers because their authors claim to present “simple” EoS (Equations of State) with what they believe to be the minimum amount of complexity appropriate for modeling thermodynamic properties of working fluids appropriate for ORC applications, which also is the goal of the current paper. However, the current paper differs from Refs. [2,3] in that it presents a much simpler approach while still being able to yield similar accuracy. Therefore, in our opinion, our approach proves to be a much more powerful methodology than that of Refs. [2,3], particularly for evaluating large numbers of not-so-well-described (little experimental data exist) working fluids.

Briefly, Refs. [2,3] modeled the thermodynamic properties of the working fluids using molecular based families of EoS such as BACKONE and PC-SAFT. They did so because they assert that only 3–5 substance-specific parameters—and thus few experimental measurements of vapor pressure and liquid densities—are needed to construct these EoS; whereas, much more accurate EoS such as the FEQ (Fundamental Helmholtz Equation) implemented in programs such as REFPROP [4] require many more substance-specific parameters—and thus require a much larger set of high-accuracy experimental measurements for their construction. Furthermore, they claim that simpler cubic EoS, such as Redlich–Kwong (R–K), Peng–Robinson (P–R), etc., which have only a few parameters—thus requiring many fewer experimental measurements—do not possess sufficient accuracy for cycle calculations. In summary, they claim their approach involves the “minimum amount” of complexity to yield sufficiently accurate results.

One major purpose of the current paper is to disagree with the claim of Refs. [2,3] and present a much simpler—yet sufficiently accurate—approach. We will demonstrate the validity and usefulness of our approach through example and illustration. In particular, we will show that using cubic EoS (P–R in our case) do in fact yield sufficient accuracy for engineering purposes and is a much more powerful approach than applying more complicated, more expensive, and more difficult to implement EoS such as BACKONE or PC-SAFT, and therefore will prove to be a much more powerful tool in examining not-so-well-described working fluids. In short, the approach presented in this paper is a fast, easy, inexpensive, and reasonably accurate method for identifying and evaluating large numbers of potential well-described and not-so-well-described working fluids for ORC applications. If these goals could be realized, they would help to increase the use of ORC, increase the mix of renewables in electricity production, lead to increased

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