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Effects of ammonia concentration on the thermodynamic performances of ammonia–water based power cycles

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ABSTRACT

The power generation systems using a binary working fluid such as ammonia–water mixture are proven to be the feasible method for utilizing a low-temperature waste heat source. In this work, ammonia–water based Rankine (AWR) regenerative Rankine (AWRR) power generation cycles are comparatively analyzed by investigating the effects of ammonia mass concentration in the working fluid on the thermodynamic performances of systems. Temperature distributions of fluid streams in the heat exchanging devices are closely examined at different levels of ammonia concentration and they might be the most important design consideration in optimizing the power systems using a binary working fluid. The analysis shows that the lower limit of workable ammonia concentration decreases with increasing turbine inlet pressure. Results also show that both the thermal and exergy efficiencies of AWRR system are generally better than those of AWR system, and can have peaks at the minimum allowable ammonia concentrations in the working range of system operation.

1. Introduction

Since worldwide energy demand has been rapidly increasing but the fossil fuel to meet the demand is being drained, an efficient use of low-temperature energy source such as geothermal energy, exhaust gas from gas turbine system, biomass combustion, or waste heat from various industrial processes becomes more and more important. For the past 20 years, the organic Rankine cycle (ORC) and the power generating system using binary mixture as a working fluid have attracted much attention as they are proven to be the most feasible methods to achieve high efficiency in converting the low-grade thermal energy to more useful forms of energy.

ORCs have been developed for the main purpose of utilizing low-temperature heat ($80\,^{\circ}\mathrm{C} < T < 300\,^{\circ}\mathrm{C}$) [1,2]. However, the thermal performance of such cycles is quite poor, since pure fluids have the properties of boiling and condensing at constant temperature, which leads to large temperature differences in the vapor generator and condenser and in turn inevitably increases the irreversibility. On the other hand, the use of ammonia–water mixture, which is a zeotropic binary-mixture, as a working fluid in the power generating system has been found to be another promising candidate for utilizing low-temperature heat source [3–6].

A major advantage for using mixtures as a working fluid in the power generation systems instead of pure working fluids is that heat can be supplied or rejected at variable temperature but still at constant pressure, since the boiling temperature now varies during the phase change and the binary mixture evaporates over a wide range of temperature. The variable-temperature heat transfer process alleviates the temperature mismatch between hot and cold streams in heat exchanging components of the system, which then reduces the exergy destruction in the power cycles. The particular use of ammonia in the binary mixture with water possesses several merits other than the fact that the ammonia is relatively inexpensive. Ammonia and water have the similar molecular weights and thus, traditional design of steam turbines can be used in the ammonia–water power cycles only with minor modifications. Also, the boiling point of ammonia is substantially lower than that of water, which makes it practically useful to utilize the low-temperature waste heat in the power generation systems [7,8].

Ibrahim [9] studied an ammonia–water Rankine cycle and found that the design of heat exchanger networks can have a significant impact on the performance of power cycles. Zamfirescu and Dincer [10] analyzed trilateral ammonia–water Rankine cycle that uses no boiler, but rather the saturated liquid is flashed by an expander. Recently, Roy et al. [11] studied ammonia–water Rankine cycle

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Nomenclature

c_p	isobaric specific heat (kJ/kg K)
e	specific exergy (kJ/kg)
e_{in}	exergy input per unit mass of source (kJ/kg)
G	specific Gibbs free energy (kJ/kmol)
h	specific enthalpy (kJ/kg)
N	number of moles (kmol)
P	pressure (bar)
P_H	turbine inlet pressure (bar)
P_L	condenser pressure (bar)
q	specific heat transfer (kJ/kg)
Q	relative heat transfer in heat exchangers
R	universal gas constant = 8.3142 kJ/kmol K
r_{ms}	mass flow ratio of mixture to source
r_{cm}	mass flow ratio of cooling water to mixture
s	specific entropy (kJ/kg K)
T	temperature (°C)
T_s	source temperature (°C)
T_{cw}	cooling water temperature (°C)
v	specific volume (m^3/kg)
w	specific work (kJ/kg)
x	mole/mass ammonia concentration
x_b	ammonia mass concentration of the system
α	fraction of vapor
ΔT	temperature difference of streams, (°C)
ΔT_s	temperature difference of streams at source inlet, (°C)
ΔT_{cw}	temperature difference of streams at cooling-water inlet, (°C)
ΔT_{pp}	pinch point, (°C)
η_{th}	thermal efficiency
η_{ex}	exergy efficiency
η_p	isentropic efficiency of pump
η_t	isentropic efficiency of turbine
μ	chemical potential

Superscripts/subscripts

0	reference state for thermodynamic properties
a	ammonia
cw	cooling water
ds	dead state
E	excess property
out	outlet
g	gas phase
l	liquid phase
m	mixture
r	reduced property
s	source
w	water

with finite size thermodynamics and their thermodynamic calculations were carried out in the context of reasonable temperature differences in the heat exchangers.

In this study, effects of ammonia concentration on the performances of ammonia–water Rankine (AWR) cycle and ammonia–water regenerative Rankine (AWRR) cycle are comparatively investigated under the conditions of maximum mass flow rate of the working fluid. The characteristics of temperature distributions of the fluid streams in the heat exchangers are illustrated with the variation of ammonia concentration. Also, a particular attention is paid for extensively studying the effects of ammonia concentration in the working fluid of binary mixture on the important system variables including net work production, mass flow rate of working fluid, and the efficiencies of the first and second laws of thermodynamics.

2. System analysis

2.1. Thermodynamic properties of ammonia–water mixture

For the ammonia–water mixtures, the thermodynamic properties and vapor–liquid equilibrium conditions have been published by many studies [12]. However, most property data for ammonia–water mixture have been produced specifically for the absorption refrigeration processes, and thermophysical data at elevated temperatures and pressures are required for the applications of ammonia–water mixture in power generations. The property calculation method with Gibbs free energy [13] and the method of equation of state [14] might be two practical methods for this purpose.

In the analysis of this work, thermodynamic properties of the mixture are evaluated by using the Gibbs free energy, while the equilibrium conditions for bubble and dew points are evaluated by using the chemical potential concept. The Gibbs free energy of a free component is as:

$$G^L = h_0 - Ts_0 + \int_{T_0}^{T} c_p dT + \int_{P_0}^{P} v dP - T\int_{T_0}^{T}\left(\frac{c_p}{T}\right)dT \tag{1}$$

where h_0, s_0, T_0, and P_0 are the specific enthalpy, specific entropy, temperature and pressure at the reference state. By using empirical relations of density and isobaric specific heat for liquid and gas phase, Gibbs free energy can be expressed as:

$$\begin{aligned} G_r^l = {} & h_{r,0}^l - T_r s_{r,0}^l - B_1(T_r - T_{r,0}) + \left(\frac{B_2}{2}\right)(T_r^2 - T_{r,0}^2) + \left(\frac{B_3}{3}\right) \\ & (T_r^3 - T_{r,0}^3) - B_1 T_r \ln\left(\frac{T_r}{T_{r,0}}\right) - \left(\frac{B_3}{2}\right)(T_r^2 - T_{r,0}^2)T_r \\ & + (A_1 + A_3 T_r + A_4 T_r^2)(P_r - P_{r,0}) + \left(\frac{A_2}{2}\right)(P_r^2 - P_{r,0}^2) \end{aligned} \tag{2}$$

$$\begin{aligned} G_r^g = {} & h_{r,0}^g - T_r s_{r,0}^g - D_1(T_r - T_{r,0}) + \left(\frac{D_2}{2}\right)(T_r^2 - T_{r,0}^2) \\ & + \left(\frac{D_3}{3}\right)(T_r^3 - T_{r,0}^3) - D_1 T_r \ln\left(\frac{T_r}{T_{r,0}}\right) - \left(\frac{D_3}{2}\right) \\ & (T_r^2 - T_{r,0}^2)T_r + T_r \ln\left(\frac{P_r}{P_{r,0}}\right) + C_1(P_r - P_{r,0}) \\ & + C_2\left(\frac{P_r}{T_r^3} - \frac{P_{r,0}}{T_{r,0}^3} + \frac{3P_{r,0}T_r}{T_{r,0}^4}\right) + \left(\frac{C_3}{3}\right) \\ & \left(\frac{P_r^3}{T_r^{11}} - \frac{12P_{r,0}^3}{T_{r,0}^{11}} + \frac{11P_{r,0}^3 T_r}{T_{r,0}^{12}}\right) \end{aligned} \tag{3}$$

for the liquid and vapor phases, respectively [14]. Here, the superscript l is for liquid and g for gas, and the subscript r denotes the reduced properties which are defined as $T_r = T/T_0$, $P_r = P/P_0$, $G_r = G/RT_0$, $h_r = h/RT_0$, $s_r = h/R$, $v_r = hP_0/RT_0$. The reference temperature and pressure, T_0 and P_0 are 100 K and 10 bar, respectively, while R is the universal gas constant of 8.3142 kJ/kmol·K.

The Gibbs excess energy evaluates the deviation of liquid mixture properties from the ideal solution behavior, and is modeled as:

$$\frac{G^E}{RT} = x(1-x)\left[F_1 + F_2(2x-1) + F_3(2x-1)^2\right] \tag{4}$$