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Thermodynamic Properties of Ammonia–Water Mixtures for Power Cycles[1]

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Power cycles with ammonia–water mixtures as working fluids have been shown to reach higher thermal efficiencies than the traditional steam turbine (Rankine) cycle with water as the working fluid. Different correlations for the thermodynamic properties of ammonia–water mixtures have been used in studies of ammonia–water mixture cycles described in the literature. Four of these correlations are compared in this paper. The differences in thermal efficiencies for a bottoming Kalina cycle when these four property correlations are used are in the range 0.5 to 3.3%. The properties for saturated liquid and vapor according to three of the correlations and available experimental data are also compared at high pressures and temperatures [up to 20 MPa and 337°C (610 K)]. The difference in saturation temperature for the different correlations is up to 20%, and the difference in saturation enthalpy is as high as 100% when the pressure is 20 MPa.

KEY WORDS: ammonia–water mixture; Kalina cycle; power cycle; thermodynamic properties.

1. INTRODUCTION

In conventional power cycles, water is used as the working fluid. One way to improve the thermal efficiency is to replace the one-component fluid with a binary fluid. Binary fluids boil and condense at increasing and decreasing temperatures, respectively. This makes it possible to keep the temperature profile of the working fluid closer to a heat source of

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decreasing temperature and a heat sink of increasing temperature. The most well-known power cycle with a binary working fluid (an ammonia–water mixture) is the Kalina cycle. This cycle has been shown to be more efficient than conventional power cycles for several applications [1–3].

In calculating the performance of the power cycles, the correlations for the thermodynamic properties of the ammonia–water mixture play an important role. The aim of this study is to investigate correlations presented in literature. Different correlations used in Kalina cycle simulations have been compared. The correlations have also been compared to available experimental data.

2. AVAILABLE CORRELATIONS FOR THERMODYNAMIC PROPERTIES

About 30 correlations found in the literature [4–31] for the thermodynamic properties of the ammonia–water mixture are presented in Fig. 1. Most of them have been developed for pressures and temperatures lower than commonly applied in power cycles. For some applications of ammonia–water cycles (direct-fired cycles), the pressure and temperature are as high as 20 MPa and 650°C (923 K), respectively. The ammonia–water mixture will then be in the vicinity of, or maybe even above, the critical point.

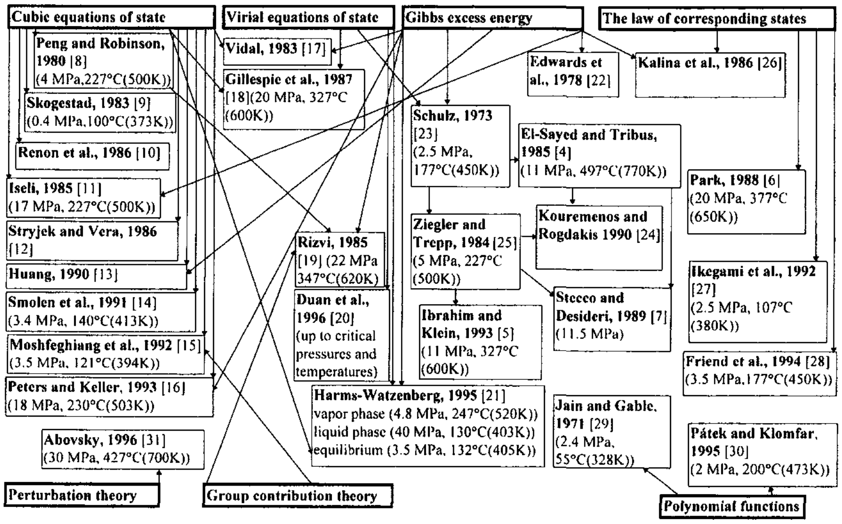

Fig. 1. Available correlations and their theoretical background. The numbers in brackets are the maximum pressure and temperature for which the correlation has been developed.

Figure 1 shows the theoretical background of the different correlations. The basis of the correlations can be divided into seven groups: cubic equations of state, virial equations of state, Gibbs excess energy, the law of corresponding states, perturbation theory, group contribution method, and polynomial functions.

Five of the correlations in Fig. 1 [4–7, 24] have been used in simulations of ammonia–water power cycles. Only the correlation by Park [6] has been developed for pressures higher than 12 MPa. This is also the only correlation using the same equations for the vapor and liquid phases. In the other correlations, different equations for the vapor and liquid phases are used. The vapor is supposed to be an ideal mixture of real gases, while the properties for the liquid phase are corrected by a term calculated from the Gibbs excess energy. In this study, the correlations by El-Sayed and Tribus [4], Park [6], Stecco and Desideri [7], and Ibrahim and Klein [5] are compared. In the correlation by El-Sayed and Tribus [4], the equations for Gibbs excess energy are taken from Schulz [23]. Stecco and Desideri [7] have combined equations from Ziegler and Trepp [25] and El-Sayed and Tribus [4]. Ibrahim and Klein [5] use the same equations as Ziegler and Trepp [25]. The constants in the function for the Gibbs excess energy have, however, been recalculated with experimental data at higher pressures and temperatures [up to 20 MPa and 316°C (589 K)]. The correlation by Park [6] consists of a generalized equation of state based on the law of corresponding states.

3. AVAILABLE EXPERIMENTAL DATA

Experimental ammonia–water mixture measurements have been reported since the beginning of the 20th century. Most of them have been performed at low temperatures and pressures. Table I shows studies performed at temperatures and pressures higher than the critical temperature and pressure of ammonia [132.4°C (405.5 K) and 11.4 MPa, respectively]. Altogether these studies give about 250 experimental points at temperatures and pressures higher than 132.4°C and 11.4 MPa.

The experimental studies have been mostly vapor–liquid equilibrium measurements. Other properties which have been measured in only a few studies are density, critical pressure and temperature, heat of mixing, and heat capacity [21, 34–36].

4. COMPARISON OF CORRELATIONS IN CYCLE SIMULATIONS

The thermal efficiencies of a Kalina cycle simulated with four correlations for the properties of the ammonia–water mixture [4–7] were compared.

Table I. Experimental Studies at Temperatures and Pressures Higher than the Critical Temperature and Pressure of Ammonia [132.4°C (405.5 K) and 11.4 MPa, Respectively].

Ref.	Year	Data	Temperature [°C (K)]	Pressure [MPa]	Mass fraction of ammonia
Postma [32]	1920	Bubble points and dew points	−77–235 (196–508)	0.0–17.8	0.1–1
Tsiklis et al. [33]	1965	Vapor–liquid equilibria	97–350 (370–623)	0–22	0–1
Rizvi [19]	1985	Vapor–liquid equilibria	33–345 (306–618)	0–22	0–1
Iseli [11]	1985	Vapor–liquid equilibria	81–220 (354–493)	3.6–16.1	0.5–0.9
Gillespie et al. [18]	1987	Vapor–liquid equilibria	40–316 (313–589)	0–21	0–1
Sassen et al. [35]	1990	Bubble points	116–340 (389–613)	1.3–21.5	0.18–0.79
		Dew points	100–180 (373–453)	0.1–9.7	0.18–0.89
Harms-Watzenberg [21]	1995	Vapor–liquid equilibria	35–225 (308–498)	0.3–17.0	0.1–1
		Liquid density	−30–140 (243–413)	0.8–37.6	0.1–0.9
		Vapor molar volume	100–200 (373–498)	0.0–4.8	0.2–0.7

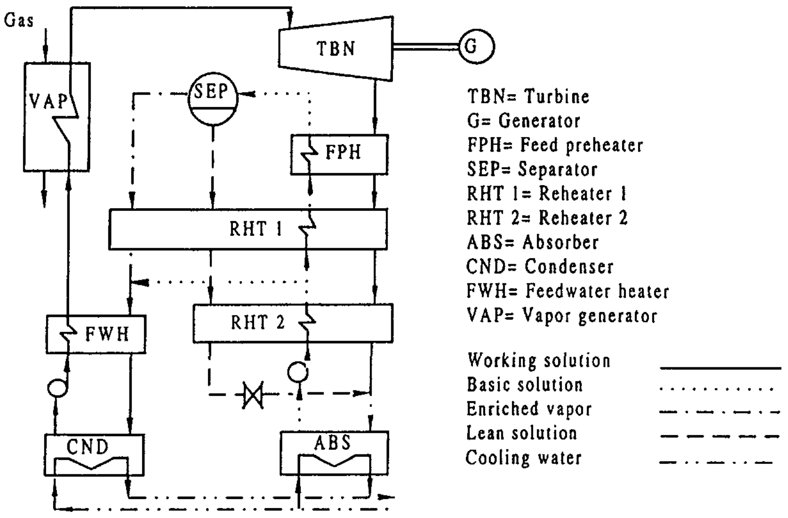

Fig. 2. Kalina cycle configuration originally presented by El-Sayed and Tribus [37].

Table II. Parameters Used in the Simulations of a Simple Kalina Cycle (Fig. 2).

Description	Value
Maximum pressure	10.8 MPa
Maximum temperature of the gas	538°C (811 K)
Minimum temperature of the gas	71°C (344 K)
Mass fraction of ammonia	
Stream through the boiler	0.70
Stream through the absorber	0.42
Heat capacity of the gas	$1.06\ \mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$
Minimum temperature difference	
Boiler outlet	28°C
Boiler pinch point	13°C
Condenser (CND)	3°C
Absorber (ABS)	3°C
Feedwater heater (FWH)	3°C
The rest of the heat exchangers	5°C

The configuration of the Kalina cycle used in the comparison is shown in Fig. 2. It was originally presented by El-Sayed and Tribus [37]. Marston [38] simulated this configuration with the correlation for the ammonia–water mixture in Ref. 4. Park and Sonntag [39] used the same configuration but with the correlation developed by Park [6]. In this study, the Kalina cycle was simulated using the correlations for the ammonia–water mixture from Stecco and Desideri [7] and Ibrahim and Klein [5]. Input data from the study by Marston [38] were used (Table II). A comparison with two higher maximum pressures in the cycle was also performed using the two latter correlations. The calculations using the correlations from Stecco and Desideri [7] were performed using the simulation program IPSEpro by Simtech, while the program EES by F-Chart Software was used for the correlations from Ibrahim and Klein [5].

Table III. The Efficiency (Net Power Generation/Heat Extracted from Heat Source) of a Simple Kalina Cycle (Fig. 2) Simulated with Different Correlations for the Properties of the Ammonia–Water Mixture.

Maximum pressure (MPa)	Stecco and Desideri [7]	Ibrahim and Klein [5]	El-Sayed and Tribus [4]	Park [6]
10.8	0.329	0.331	0.331	0.340
15.0	0.345	0.,348	Not calculated	Not calculated
20.0	0.360	0.368	Not calculated	Not calculated

The results of the comparisons are shown in Table III. With a maximum pressure of 10.8 MPa in the cycle, the differences in thermal efficiencies are in the range 0.5 to 3.3%. The correlation of Park [6] gives the highest, and the correlation of Stecco and Desideri [7] the lowest, efficiency. The efficiencies for the cycle with the three correlations based on almost the same theory are very close. With a higher maximum pressure in the cycle the difference between the correlations is still small, even though it increases. The fit of the function for Gibbs excess energy to experimental data at higher temperatures and pressures performed by Ibrahim and Klein [5] seems not to affect the efficiency of the cycle to any great extent.

5. COMPARISON OF SATURATION PROPERTIES

Comparison of saturation properties up to 250°C (523 K) calculated with different correlations have been presented in the literature [5, 40]. In this study, bubble-point and dew-point temperatures and enthalpies according to three of the correlations for properties of ammonia–water mixtures [5–7] were compared at two pressures, 11 and 20 MPa, respectively. The data for the correlation of Park [6] were taken from tables in Ref. 41. Available experimental data have been included in the comparison. A comparison of pressures and enthalpies for bubble points and

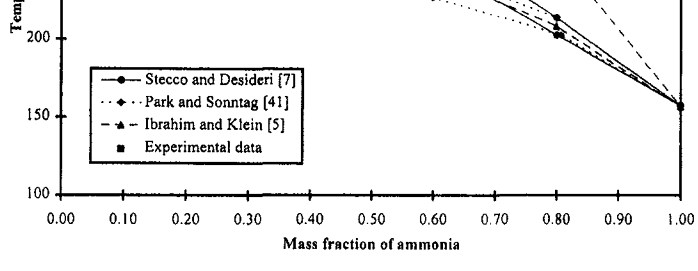

Fig. 3. Temperature for bubble points and dew points at pressure 20 MPa. The experimental data are taken from Refs. 18, 19, and 35.

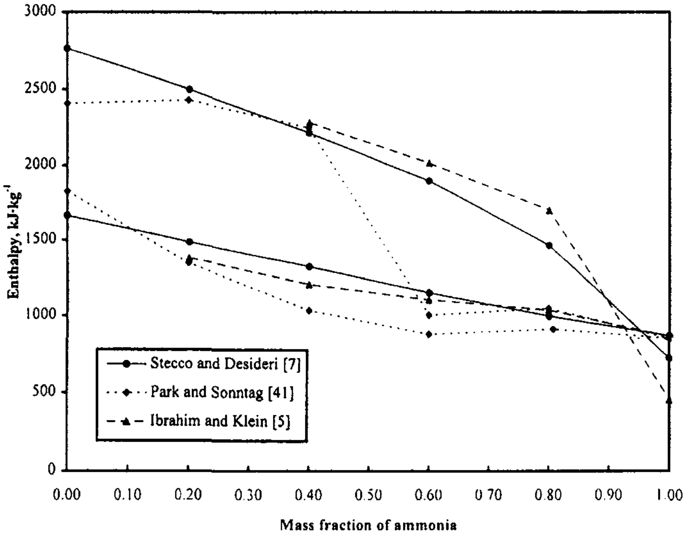

Fig. 4. Enthalpy for bubble points and dew points at pressure 20 MPa.

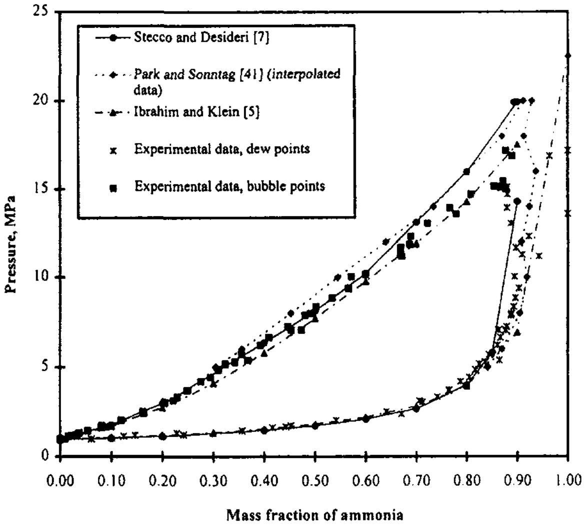

Fig. 5. Pressure for bubble points and dew points at temperature 177°C (450 K). The experimental data are taken from Refs. 11, 18, 19, 21, and 35.

dew points at temperatures from 177°C (450 K) to 337°C (610 K) was also performed.

In the comparison of the correlations at a fixed pressure, the highest pressure gives the largest difference in temperature and this occurs at high mass fractions of ammonia. The difference is at most about 20% at 20 MPa and about 9% at 11 MPa. The largest difference in enthalpy is as high as 100% at 20 MPa, while it is about 30% at 11 MPa. The experimental data for the liquid phase temperature follow the correlations of Stecco and Desideri [7] and Ibrahim and Klein [5] well at the lower pressure. At the higher pressure, experimental data are scarce. Figures 3 and 4 show the result for 20 MPa.

At a fixed temperature, the differences in enthalpy are much smaller than at a fixed pressure and reach at the most about 15%. Figures 5 and 6 show the comparison of pressures at 177 and 337°C. The correlations for the dew points follow each other well at lower mass fractions of ammonia, but at higher mass fractions the correlation of Stecco and Desideri begins to deviate from the other correlations and the differences in pressure become very large. The higher the temperature, the lower is the mass fraction of ammonia at which deviations appear, and the deviations increase with increasing mass fraction. The differences between the correlations are mostly larger than the differences between the correlations and the experimental data.

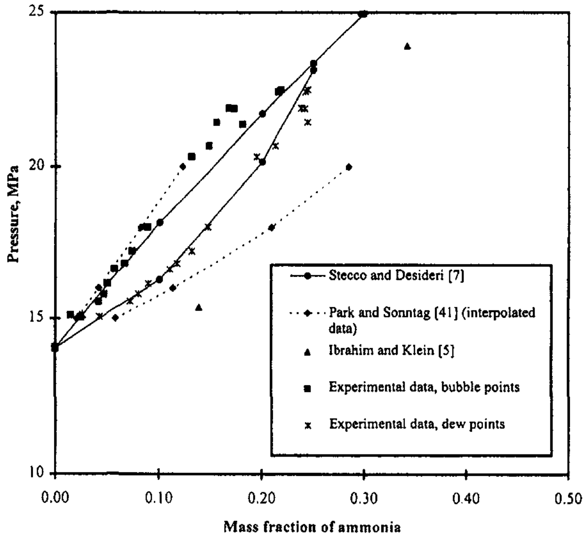

Fig. 6. Pressure for bubble points and dew points at temperature 337°C (610 K). The experimental data are taken from Refs. 19 and 35.

6. CONCLUSIONS

Most of the correlations for the properties of ammonia-water mixtures found in the literature have been developed for lower temperatures and pressures than those common in power cycles. There are very few experimental data at high temperatures and pressures and most of them are vapor-liquid equilibrium data. To achieve accurate correlations at high temperatures and pressures, more experimental data are necessary.

The correlations for the properties of ammonia-water mixtures used in simulations of power cycles have not been developed for high temperatures and pressures. When used in simulations of a simple Kalina cycle, different correlations give cycle efficiencies with a difference not higher than 0.5 to 3.3%. The differences in saturation properties between the correlations are, however, considerable at high pressures, high temperatures and high mass fractions of ammonia. In some power cycle applications, the pressure and temperature are as high as 20 MPa and 650°C, respectively. The mixture will then be in the vicinity of, or above, the critical point. In order to accomplish reliable simulations of the power cycles, new experimental data and correlations are desired.

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