

Comparison of Correlations for Predicting Thermodynamic Properties of Ammonia–Water Mixtures

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Received August 25, 1999

Tillner-Roth and Friend have presented a new correlation for the thermodynamic properties of ammonia–water mixtures. In this study, the new correlation has been compared to other correlations used in simulations of power cycles using ammonia–water mixtures as working fluids. The saturation properties for mixtures, calculated with the different correlations, have been examined at different temperatures and pressures. Available experimental data have been included in the comparison. The variation of the enthalpy with temperature at different pressures for a mixture has also been compared. The correlations have been examined for use in power cycle simulations as well. The comparison reveals that the new correlation shows a more reasonable behavior when the critical point of the mixture is approached. At lower temperatures and pressures, the compared correlations give very similar results. The differences in the results from the cycle simulations, using different correlations, are small but they tend to increase with increasing maximum pressure in the cycle.

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

1. INTRODUCTION

In conventional steam 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. While heat exchanging, this makes it possible to keep the temperature profile of the working fluid closer to a

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heat source of 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].

For theoretical performance simulations of ammonia–water power cycles, thermodynamic properties are necessary. A previous study [4] shows that there are several correlations available for the mixture, but very few have been developed for the high pressures and temperatures appearing in power cycles.

In 1998, a new correlation for the ammonia–water mixture was presented by Tillner-Roth and Friend [5]. In the present study, this correlation is compared to two other correlations previously used in power cycle simulations. The predicted saturation properties for the mixture have been compared at three different temperatures and pressures. The variation of the enthalpy with temperature at different pressures for a mixture with the mass fraction of ammonia 0.7 has also been examined using the different correlations. Finally, power cycle simulations have been performed to show the sensitivity of thermal efficiencies to the choice of correlation.

2. THERMODYNAMIC PROPERTIES CORRELATIONS

In previous studies of power cycles presented by the present author [2, 6], a correlation for the thermodynamic properties of the ammonia–water mixture developed by Stecco and Desideri [7] was used. Their correlation is based on work presented by Ziegler and Trepp [8] and El-Sayed and Tribus [9]. Expressions for the Gibbs free energy, for which pressure, temperature, and mole fraction of ammonia are independent variables, are used as the fundamental function. Different equations are used for the vapor and liquid phases. The vapor is assumed to be an ideal mixture of real gases, while the properties of the liquid phase are corrected by a term calculated from the Gibbs excess energy. Equations (1) and (2) illustrate the formulations of the equations for the vapor phase and liquid phase, respectively. Here, g is the molar Gibbs energy, x the mole fraction of ammonia, T the temperature, p the pressure, and R the universal gas constant. The superscripts l and v indicate liquid phase and vapor phase, respectively, and g_E is the Gibbs excess energy.

$$g^l(T, p, x) = (1 - x) g_{\text{H}_2\text{O}}^l(T, p) + x g_{\text{NH}_3}^l(T, p) + RT[(1 - x) \ln(1 - x) + x \ln x] + g_E(T, p, x) \quad (1)$$

$$g^v(T, p, x) = (1 - x) g_{\text{H}_2\text{O}}^v(T, p) + x g_{\text{NH}_3}^v(T, p) + RT[(1 - x) \ln(1 - x) + x \ln x] \quad (2)$$

The functions presented by Ziegler and Trepp have been correlated to experimental data for the mixture up to 210°C (483 K) and 3.5 MPa, while El-Sayed and Tribus have taken into account data up to 316°C (589 K) and 20 MPa. The maximum pressure for the correlations from Stecco and Desideri has been set at 11.5 MPa, which is slightly above the critical pressure of ammonia. The same correlations as suggested by Stecco and Desideri have also been presented and used by Xu and Goswami [10].

Another correlation, also used in power cycle simulations, is the one presented by Ibrahim and Klein [11]. They use the same equations as Ziegler and Trepp [8]. 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)]. In the previous study of the present author [4], two other correlations [9, 12], used in power cycle calculations, were compared to the correlations presented by Stecco and Desideri and Ibrahim and Klein.

The new correlation presented by Tillner-Roth and Friend is based on a fundamental equation of state for the Helmholtz free energy using the equation of state for water by Pruss and Wagner [13] and a fundamental equation of state for ammonia by Tillner-Roth et al. [14]. In the new correlation, the entire thermodynamic space of the mixture is described by one single equation, and the independent variables are volume, temperature, and mole fraction of ammonia. The formulation of the equation is illustrated by Eq. (3), where a is the molar Helmholtz free energy and v is the molar volume. The superscript r stands for residual.

$$a(T, v, x) = (1 - x) a_{\text{H}_2\text{O}}(T, v) + x a_{\text{NH}_3}(T, v) + RT[(1 - x) \ln(1 - x) + x \ln x] + \Delta a^r(T, v, x) \quad (3)$$

The functions for the pure components, $a_{\text{H}_2\text{O}}$ and a_{NH_3} , consist of a function for ideal-gas properties and a residual part correcting to the real-component behavior. The term for the departure from nonideal mixture behavior, $\Delta a^r(T, v, x)$, is correlated with the most reliable, available experimental data for the ammonia–water mixture and also with data for the critical region from a modified Leung–Griffiths model which is known to be able to describe vapor–liquid equilibria for mixtures in the critical region [5]. It should be pointed out that dimensionless forms of the temperature and volume are used in the equations for the pure components presented by Pruss and Wagner and Tillner-Roth et al. Reduced properties are used in the correlations for the ammonia–water mixture as well.

For a mixture liquid and vapor phase in equilibrium, the chemical potential of each component is the same in both the liquid and the vapor

phase. By setting up equations for this equality and solving them iteratively, the saturation properties for the mixture can be calculated. In the correlations both by Ibrahim and Klein and by Tillner-Roth and Friend, this procedure for calculating the saturation properties is used. Stecco and Desideri instead use empirical functions from El-Sayed and Tribus [9] for calculation of the bubble-point and dew-point temperatures.

Finally, it should be noted that in the correlation by Tillner-Roth and Friend, a different reference state for ammonia is used than in the other correlations. Therefore enthalpies and entropies calculated from the different correlations cannot be directly compared.

3. COMPARISON OF PROPERTY PREDICTIONS

The correlations described above have been employed to calculate saturation pressures and enthalpies, as well as enthalpy, for ammonia–water mixtures. These predictions of the properties by the different correlations have then been compared. Experimental data have also been included in the comparison when available. To carry out the comparison, the reference state for ammonia has been changed in the Tillner-Roth and Friend correlation, so that it is the same as the state used in the correlations presented by Stecco and Desideri [7] and Ibrahim and Klein [11].

The variation of the saturation pressure and enthalpy with mass fraction of ammonia has been examined at three temperatures: 177°C (450 K), 247°C (520 K), and 337°C (610 K). Experimental data from Refs. 15–19 have also been included. Predictions of saturation enthalpies at three pressures (10.82, 15, and 18 MPa), the maximum pressures used in the simulation of the power cycle, have also been compared, as has the variation of the enthalpy with temperature at four pressures (10.82, 15, 18, and 20 MPa) for a mixture with 70% ammonia, by weight.

4. COMPARISON OF CORRELATIONS IN POWER CYCLE SIMULATION

The thermal efficiencies for a power cycle simulated with the different correlations for the working fluid properties have been compared at three maximum pressures (10.82, 15, and 18 MPa). The power cycle simulated is a Kalina cycle (Fig. 1) originally presented by El-Sayed and Tribus [20], which is the same cycle used in the previous study by the author [4]. The same input data (Table I) as in the previous study have been used in the present study with one minor exception: in this study all minimum temperature differences in the heat exchangers have been set at 3°C instead of 3°C for some heat exchangers and 5°C for others, as was done earlier.

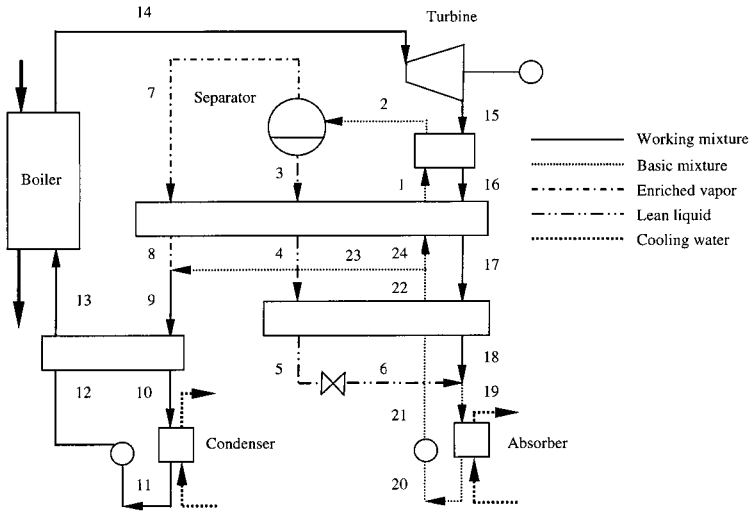


Fig. 1. The Kalina cycle simulated in the comparison of the correlations. The configuration was originally presented by El-Sayed and Tribus [20].

Another difference in this study, compared to the previous study, is that an optimization of the thermal efficiency has been performed for each simulation by varying the mass fraction of ammonia for the working and basic mixtures. In the previous work, the simulations were performed with the same mass fraction of ammonia for the working mixture, for all correlations of the working fluid properties.

The calculations were performed using the simulation programs IPSEpro by Simtech and EES (Engineering Equation Solver) by F-Chart Software.

Table I. Parameters Used in the Simulations of a Simple Kalina Cycle (Fig. 1)

Description	Value
Maximum temperature of the gas	538°C (811 K)
Minimum temperature of the gas	70.54°C (343.69 K)
Heat capacity of gas	1.058 kJ · kg ⁻¹ · K ⁻¹
Temperature of	
Incoming cooling water	12.8°C (285.95 K)
Outgoing cooling water	23.9°C (297.05 K)
Minimum temperature difference	
Boiler outlet	28°C
Boiler pinch point	13°C
Heat exchangers	3°C

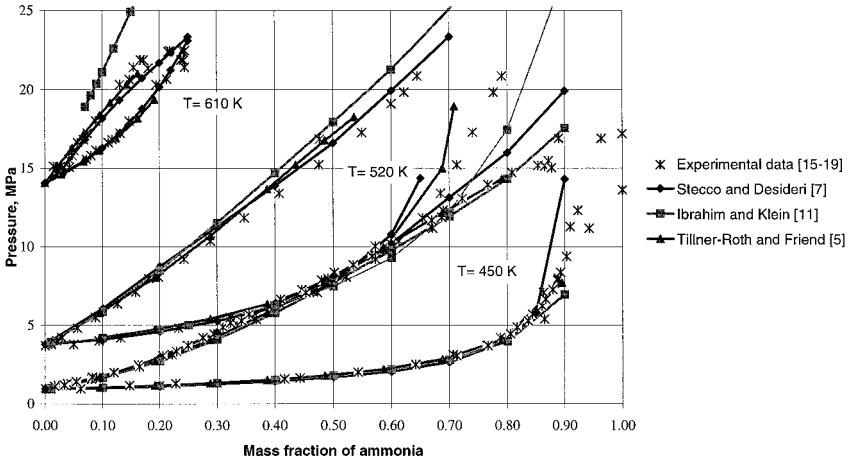


Fig. 2. Pressures for bubble points and dew points versus ammonia mass fraction and temperature.

5. RESULTS

The comparison of the predicted saturation properties is shown in Figs. 2 to 6. As shown, for the lowest temperature, the correlations give very similar saturation properties. The correlation from Tillner-Roth and Friend shows a slightly better agreement with the experimental data

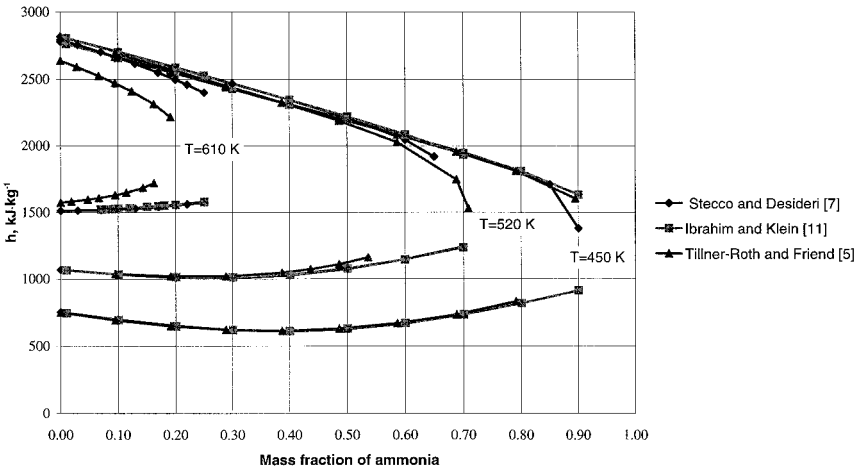


Fig. 3. Enthalpy for bubble points and dew points versus ammonia mass fraction and temperature.

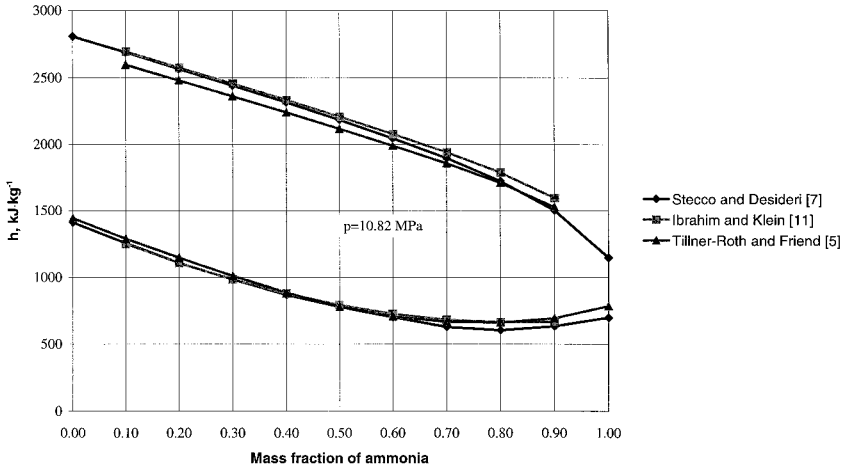


Fig. 4. Enthalpy for bubble points and dew points at pressure 10.82 MPa.

(Fig. 2). At higher temperatures, the correlations still show good agreement in saturation pressure, except for the correlation from Ibrahim and Klein at 337°C (610 K). The bubble-point pressures from this correlation are much higher and also show some fluctuations. At 610 K, dew properties cannot be calculated with the calculation routine, for the correlation from Ibrahim and Klein, in EES and can therefore not be found in the figures.

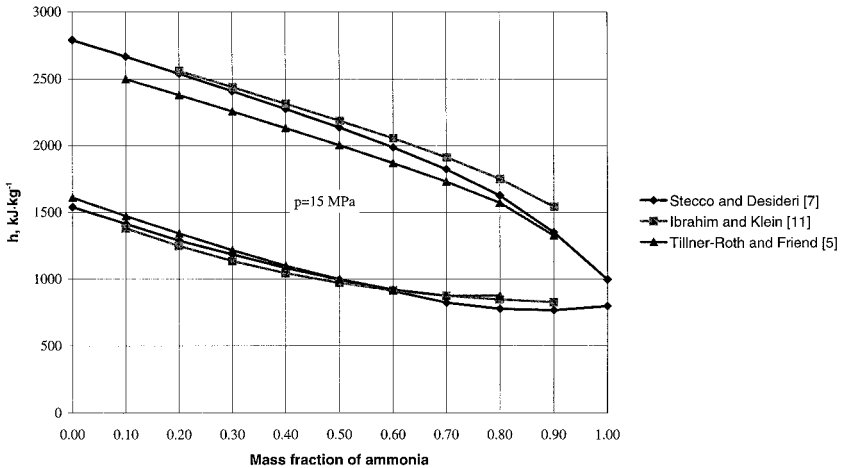


Fig. 5. Enthalpy for bubble points and dew points at pressure 15 MPa.

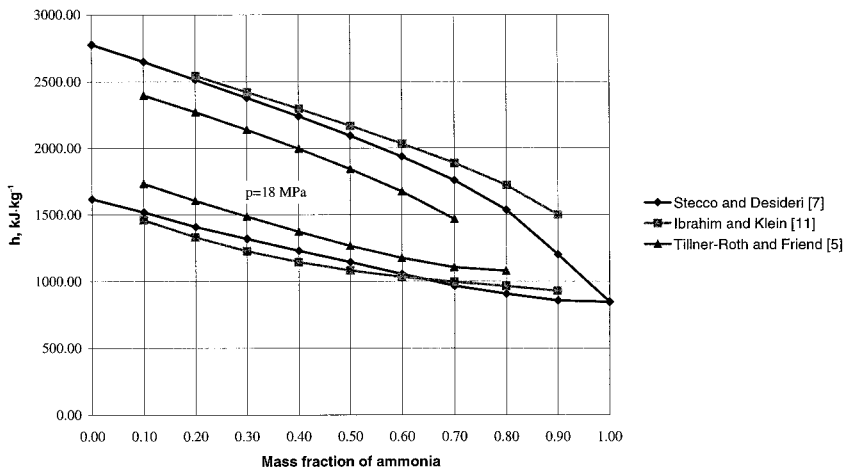


Fig. 6. Enthalpy for bubble points and dew points at pressure 18 MPa.

For the saturation enthalpies (Fig. 3), the two-phase envelope is smaller for the correlation from Tillner-Roth and Friend than for the other correlations. At the highest temperature, the difference in predicted saturation enthalpy is at most about 12%. At constant pressure, the differences in the enthalpy increase with pressure. Again, the two-phase envelopes are smaller for the correlation by Tillner-Roth and Friend. The largest difference in predicted enthalpy is about 8% at the lowest pressure (Fig. 4), increasing to about 25% at the highest pressure (Fig. 6). It should be pointed out that some fluctuations in the enthalpies can occur for high mass fractions of ammonia (higher than 0.65) at the highest pressure when the calculation routine for the correlation by Tillner-Roth and Friend is used. Here an increase in the ammonia mass fraction in small steps gives jumps in the enthalpy instead of a smooth decrease.

The results for the comparison of the properties for a mixture with a mass fraction of ammonia of 0.7 are shown in Fig. 7. At the lowest pressure, the correlations show very similar behavior. At higher pressures, which, according to the measured critical pressures presented by Sassen et al. [19], should be in the critical region, the correlations show different behavior. While the correlation by Stecco and Desideri shows a steep change in the enthalpy, the correlation by Tillner-Roth and Friend shows a smoother change. The correlation by Ibrahim and Klein gives a smoother change in the enthalpy than the correlation by Stecco and Desideri, but it is steeper than the change shown by the correlation by Tillner-Roth and Friend. Since there are no phase changes above the critical point, the smooth change in the properties seems to be more reasonable.

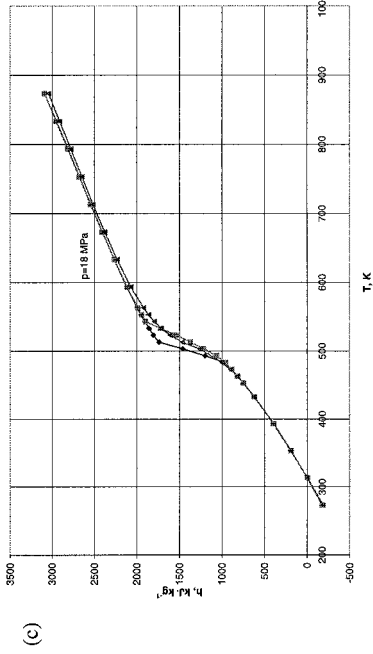
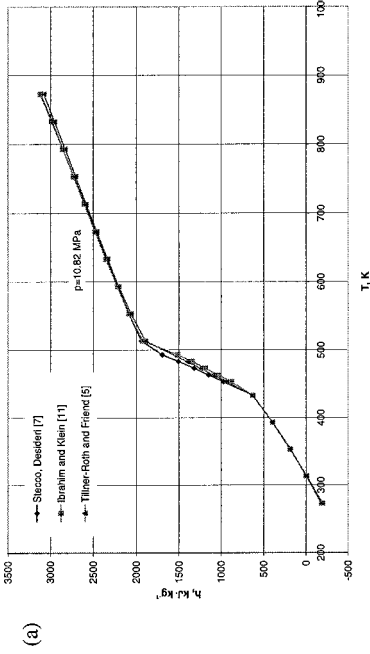
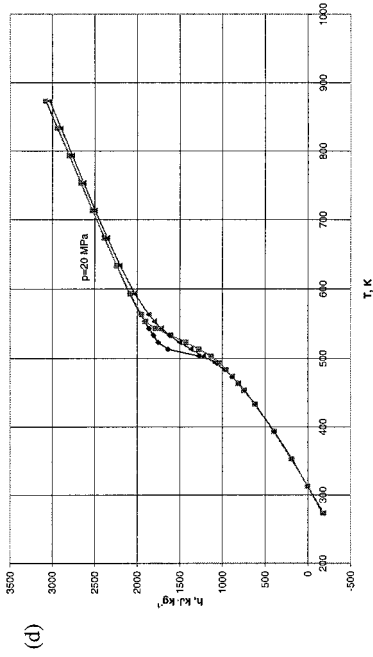
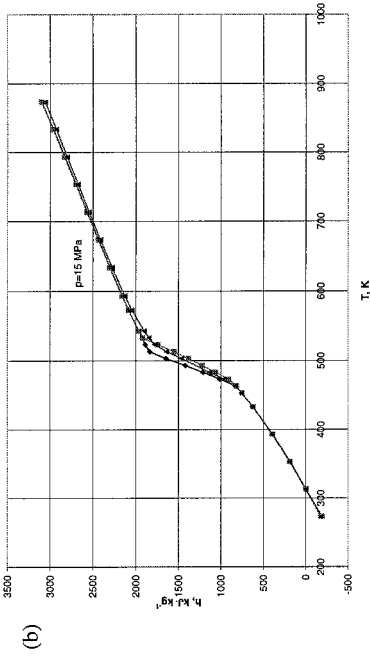


Fig. 7. The variation of enthalpy with temperature for a mixture with mass fraction of ammonia of 0.7 (a) at 10.82 MPa, (b) at 15 MPa, (c) at 18 MPa, and (d) at 20 MPa.

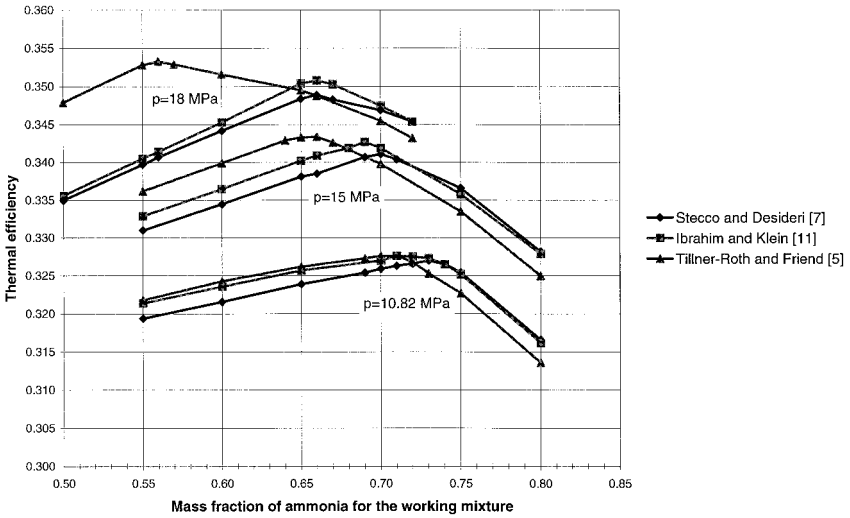


Fig. 8. The variation of the first law efficiency with mass fraction of ammonia for the working mixture when the configuration of the Kalina cycle, shown in Fig. 1, is simulated with different correlations for the thermodynamic properties.

The results of the comparison in the cycle simulations are shown in Fig. 8. The differences in the optimized efficiencies are small (at most about 1%) and the correlation from Tillner-Roth and Friend gives the highest efficiencies. The differences increase with a higher maximum pressure in the cycle. The differences in the mass fraction of ammonia for the working mixture, giving the maximum thermal efficiency, also increase with maximum pressure in the cycle. Here the difference in the mass fraction of ammonia is as large as 0.10 for the highest pressure. The correlation of Tillner-Roth and Friend gives a maximum thermal efficiency at a lower mass fraction of ammonia than the other correlations.

For a specified mass fraction of ammonia in the working mixture, the difference in efficiency can be higher than for the optimized efficiencies. Still, the difference seems not to be higher than about 4%. The difference in efficiency for simulations with high mass fractions of ammonia for the working mixture is similar for the three pressures. For low mass fractions of ammonia for the working mixture, the difference in efficiency increases with pressure.

In Table II, some results from simulations with the same ammonia mass fraction of the working mixture are listed, and in Table III, all state points of the cycle are listed for the simulations with an ammonia mass fraction of the working mixture of 0.65. For each correlation, the ammonia mass fraction of

the basic mixture has been varied to achieve the optimal power output. However, the maximum thermal efficiency is achieved with about the same ammonia mass fraction of the basic mixture, and the pressure after the turbine is also very similar. The enthalpy of the working fluid after the turbine is always lower for the correlations developed by Tillner-Roth and Friend and the difference is about the same for all three pressures. The same is valid for the enthalpy for the working fluid before the turbine, but here the difference increases slightly with a higher maximum pressure in the cycle. The enthalpies before and after the turbine are very similar for the correlations by Stecco and Desideri and Ibrahim and Klein.

The differences in enthalpy for the subcooled liquid before the boiler from the three correlations are very small. For the bubble-point enthalpies, the differences are larger. As can be seen in Figs. 4–6, the correlation giving the highest and lowest bubble-point enthalpy varies with the mass fraction of ammonia.

6. DISCUSSION

One important difference among the correlations studied here is that the correlation by Tillner-Roth and Friend includes corrections for nonideal mixture behavior for all phases, while the other two correlations consider the vapor phase to be an ideal mixture. This may be a reason why the largest difference in the predictions of the saturation properties is observed for the dew points at high pressures, where the ideal-mixture assumption should be the least correct. Another difference that could be expected to influence the results at high pressures and temperatures is the inclusion of data from the Leung-Griffith model in the establishment of the correlation by Tillner-Roth and Friend. The fact that different experimental data have been used in the formulation of the different correlations could also contribute to the differences in the predicted properties.

The problems in calculating saturation properties with the Ibrahim and Klein correlations could be due to the fact that the equations for the vapor–liquid equilibrium must be solved iteratively. Using the correlations by Stecco and Desideri also includes iterations when the temperature and mass fraction of ammonia are known, but since the equations for the bubble-point and dew-point temperatures are used, the computation routine is simple. The fluctuations in predicted enthalpy from the correlations by Tillner-Roth and Friend at constant pressures appear for mass fractions of ammonia in the critical region. According to measurements of critical pressures presented by Sassen et al. [19], 18 MPa is the critical pressure for a mixture with a mass fraction of ammonia of about 0.68.

Table II. Results from the Cycle Simulations

	$W_{\text{work}} = 0.55$				$W_{\text{work}} = 0.60$				$W_{\text{work}} = 0.65$				$W_{\text{work}} = 0.70$				$W_{\text{work}} = 0.75$					
	TF ^b	SD	IK	TF	SD	IK	TF	SD	IK	TF	SD	IK	TF	SD	IK	TF	SD	IK	TF	SD	IK	
η (%) ^a	32.2	31.9	32.1	32.4	32.2	32.4	32.6	32.4	32.6	32.8	32.6	32.7	32.3	32.5	32.5	32.5	32.5	32.5	32.5	32.5	32.5	32.5
W_{19}	0.312	0.317	0.317	0.344	0.351	0.350	0.379	0.386	0.385	0.418	0.423	0.425	0.466	0.464	0.471	0.466	0.464	0.464	0.466	0.464	0.471	0.471
p_{15} (MPa)	0.07	0.07	0.07	0.09	0.09	0.08	0.11	0.11	0.11	0.14	0.15	0.14	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19
h_{15}	1929	1943	1939	1911	1927	1923	1895	1911	1908	1881	1896	1896	1873	1883	1886	1873	1883	1886	1873	1883	1886	1886
(kJ · kg ⁻¹)																						
h_{14}	2923	2945	2949	2882	2905	2908	2840	2864	2867	2799	2823	2826	2758	2783	2786	2758	2783	2786	2758	2783	2786	2786
(kJ · kg ⁻¹)																						
h_{13}	5	6	8	17	17	20	28	27	32	37	37	42	42	46	49	42	46	49	42	46	49	49
(kJ · kg ⁻¹)																						
h_{13b}	738	740	757	705	700	725	682	661	700	666	628	681	659	607	669	659	607	669	659	607	669	669
(kJ · kg ⁻¹)																						

 $p_{\text{max}} = 10.82$ MPa

$p_{\max} = 15.00 \text{ MPa}$

η^a	33.6	33.1	33.3	34.0	33.5	33.7	34.3	33.8	34.0	34.0	34.1	34.2	33.4	33.7	33.6
w_{19}	0.316	0.320	0.321	0.349	0.355	0.354	0.385	0.391	0.391	0.426	0.429	0.432	0.476	0.474	0.481
P_{15}	0.07	0.07	0.07	0.09	0.09	0.09	0.12	0.12	0.11	0.15	0.15	0.15	0.21	0.20	0.20
h_{15}	1871	1887	1883	1860	1872	1868	1839	1857	1854	1827	1843	1820	1833	1837	1837
h_{14}	2888	2915	2919	2848	2876	2880	2808	2837	2840	2769	2798	2801	2729	2759	2761
h_{13}	4	6	7	15	16	19	25	25	29	32	35	38	40	43	44
h_{13b}	957	954	942	921	910	916	893	864	893	874	822	875	868	792	860

 $p_{\max} = 18.00 \text{ MPa}$

η^a	35.3	34.0	34.1	35.2	34.4	34.5	35.0	34.8	35.0	34.6	34.7	34.8	n.c.	n.c.	n.c.
w_{19}	0.318	0.322	0.322	0.352	0.358	0.357	0.388	0.395	0.394	0.430	0.433	0.436	n.c.	n.c.	n.c.
P_{15}	0.07	0.07	0.07	0.09	0.09	0.09	0.12	0.12	0.12	0.16	0.16	0.15	n.c.	n.c.	n.c.
h_{15}	1837	1854	1851	1820	1840	1836	1805	1826	1822	1794	1812	1812	n.c.	n.c.	n.c.
h_{14}	2862	2892	2897	2823	2855	2859	2785	2818	2821	2747	2780	2782	n.c.	n.c.	n.c.
h_{13}	4	6	8	14	15	18	24	24	28	31	33	37	n.c.	n.c.	n.c.
h_{13b}	1135	1100	1055	1103	1055	1033	1083	1009	1013	1079	966	996	n.c.	n.c.	n.c.

^a The subscripts refer to the stream numbers in Fig. 1 and b is the boiling point of the stream, w is the mass fraction of ammonia, η is the thermal efficiency, p is the pressure, and h is the enthalpy.

^b The abbreviations have the following meaning: TF, correlation for the thermodynamic properties by Tillner-Roth and Friend [5]; SD, correlation for the thermodynamic properties by Stecco and Desideri [7]; IK, correlation for the thermodynamic properties by Ibrahim and Klein [11]. n.c., not calculated.

Table III. The State Points of the Cycle for the Simulations with $x_{\text{work}} = 0.65$

Tillner-Roth and Friend [5]										Stecco and Desideri [7]										Ibrahim and Klein [11]									
No. ^a	T (K) ^b	p (MPa)	m (kg · s ⁻¹)	w (kg · kg ⁻¹)	h (kJ · kg ⁻¹)	T (K)	p (MPa)	m (kg · s ⁻¹)	w (kg · kg ⁻¹)	h (kJ · kg ⁻¹)	T (K)	p (MPa)	m (kg · s ⁻¹)	w (kg · kg ⁻¹)	h (kJ · kg ⁻¹)	T (K)	p (MPa)	m (kg · s ⁻¹)	w (kg · kg ⁻¹)	h (kJ · kg ⁻¹)									
$P_{\text{max}} = 10.82 \text{ MPa}$																													
1	340	0.430	3.52	0.379	219	337	0.428	3.56	0.386	191	342	0.427	3.33	0.385	258														
2	345	0.430	3.52	0.379	301	343	0.428	3.56	0.386	288	346	0.427	3.33	0.385	325														
3	345	0.430	3.04	0.290	113	343	0.428	3.10	0.301	288	346	0.427	2.85	0.292	329														
4	330	0.430	3.04	0.290	47	330	0.428	3.10	0.301	50	331	0.427	2.85	0.292	329														
5	293	0.430	3.04	0.290	-120	293	0.428	3.10	0.301	-126	293	0.427	2.85	0.292	-102														
6	293	0.112	3.04	0.290	-120	293	0.115	3.10	0.301	-126	293	0.109	2.85	0.292	-102														
7	345	0.430	0.48	0.947	1497	343	0.428	0.46	0.954	1482	346	0.427	0.47	0.944	1507														
8	330	0.430	0.48	0.947	1355	330	0.428	0.46	0.954	1361	331	0.427	0.47	0.944	1355														
9	328	0.430	1.00	0.650	649	328	0.428	1.00	0.650	637	329	0.427	1.00	0.650	652														
10	316	0.430	1.00	0.650	480	316	0.428	1.00	0.650	479	316	0.427	1.00	0.650	488														
11	289	0.430	1.00	0.650	-149	289	0.428	1.00	0.650	-140	289	0.427	1.00	0.650	-141														
12	289	0.82	1.00	0.650	-141	289	0.82	1.00	0.650	-131	289	0.82	1.00	0.650	-131														
13	325	0.82	1.00	0.650	28	324	0.82	1.00	0.650	27	325	0.82	1.00	0.650	32														
14	783	0.82	1.00	0.650	2840	783	0.82	1.00	0.650	2864	783	0.82	1.00	0.650	2867														
15	362	0.112	1.00	0.650	1895	370	0.115	1.00	0.650	1911	367	0.109	1.00	0.650	1908														
16	345	0.112	1.00	0.650	1608	337	0.115	1.00	0.650	1565	346	0.109	1.00	0.650	1685														
17	331	0.112	1.00	0.650	1121	330	0.115	1.00	0.650	1153	331	0.109	1.00	0.650	1142														
18	321	0.112	1.00	0.650	939	323	0.115	1.00	0.650	980	322	0.109	1.00	0.650	963														
19	306	0.112	4.04	0.379	142	306	0.115	4.10	0.386	144	307	0.109	3.85	0.385	174														
20	289	0.112	4.04	0.379	-166	289	0.115	4.10	0.386	-168	289	0.109	3.85	0.385	-152														
21	289	0.430	4.04	0.379	166	289	0.428	4.10	0.386	168	289	0.427	3.85	0.385	-151														
22	327	0.430	4.04	0.379	4	327	0.428	4.10	0.386	8	328	0.427	3.85	0.385	17														
23	327	0.430	0.52	0.379	4	327	0.428	0.54	0.386	8	328	0.427	0.53	0.385	17														
24	327	0.430	3.52	0.379	4	327	0.428	3.56	0.386	8	328	0.427	3.33	0.385	17														
$P_{\text{max}} = 15.00 \text{ MPa}$																													
1	340	0.430	3.26	0.385	229	340	0.428	3.05	0.391	254	342	0.427	3.09	0.391	267														
2	345	0.430	3.26	0.385	314	345	0.428	3.05	0.391	332	346	0.427	3.09	0.391	328														
3	345	0.430	2.78	0.290	113	345	0.428	2.58	0.291	122	346	0.427	2.62	0.292	339														
4	329	0.430	2.78	0.290	42	329	0.428	2.58	0.291	50	330	0.427	2.62	0.292	58														
5	293	0.430	2.78	0.290	-118	293	0.428	2.58	0.291	-122	293	0.427	2.62	0.292	-102														
6	293	0.116	2.78	0.290	-118	293	0.119	2.58	0.291	-122	293	0.114	2.62	0.292	-102														
7	345	0.430	0.47	0.947	1497	346	0.428	0.47	0.947	1495	345	0.427	0.47	0.944	1507														
8	329	0.430	0.47	0.947	1347	329	0.428	0.47	0.947	1339	330	0.427	0.47	0.944	1347														
9	327	0.430	1.00	0.650	634	327	0.428	1.00	0.650	626	327	0.427	1.00	0.650	636														

10	315	0.430	1.00	0.650	471	315	0.428	1.00	0.650	473	316	0.427	1.00	0.650	479
11	289	0.430	1.00	0.650	-149	289	0.428	1.00	0.650	-149	289	0.427	1.00	0.650	-141
12	289	15.00	1.00	0.650	-138	289	15.00	1.00	0.650	-128	289	15.00	1.00	0.650	-128
13	323	15.00	1.00	0.650	25	324	15.00	1.00	0.650	25	324	15.00	1.00	0.650	29
14	783	15.00	1.00	0.650	2808	783	15.00	1.00	0.650	2837	783	15.00	1.00	0.650	2840
15	350	0.116	1.00	0.650	1839	350	0.119	1.00	0.650	1857	350	0.114	1.00	0.650	1854
16	345	0.116	1.00	0.650	1564	346	0.119	1.00	0.650	1621	350	0.114	1.00	0.650	1636
17	330	0.116	1.00	0.650	1081	329	0.119	1.00	0.650	1113	330	0.114	1.00	0.650	1104
18	320	0.116	1.00	0.650	904	322	0.119	1.00	0.650	945	321	0.114	1.00	0.650	931
19	307	0.116	3.78	0.385	151	308	0.119	3.58	0.391	175	308	0.114	3.62	0.391	183
20	289	0.116	3.78	0.385	-168	289	0.119	3.58	0.391	-168	289	0.114	3.62	0.391	-154
21	289	0.430	3.78	0.385	-168	289	0.428	3.58	0.391	-168	289	0.427	3.62	0.391	-154
22	326	0.430	3.78	0.385	-2	326	0.428	3.58	0.391	3	326	0.427	3.62	0.391	10
23	326	0.430	0.53	0.385	-2	326	0.428	0.53	0.391	3	326	0.427	0.53	0.391	10
24	326	0.430	3.26	0.385	-2	326	0.428	3.05	0.391	3	326	0.427	3.09	0.391	10
$p_{\max} = 18.00 \text{ MPa}$															
1	342	0.430	3.02	0.388	264	340	0.428	2.91	0.395	260	344	0.427	2.87	0.394	305
2	346	0.430	3.02	0.388	336	345	0.428	2.91	0.395	340	347	0.427	2.87	0.394	360
3	346	0.430	2.55	0.285	119	345	0.428	2.44	0.291	122	347	0.427	2.40	0.287	135
4	329	0.430	2.55	0.285	41	328	0.428	2.44	0.291	46	329	0.427	2.40	0.287	58
5	293	0.430	2.55	0.285	-118	293	0.428	2.44	0.291	-122	293	0.427	2.40	0.287	-100
6	293	0.119	2.55	0.285	-118	293	0.122	2.44	0.291	-122	293	0.116	2.40	0.287	-100
7	346	0.430	0.47	0.944	1503	345	0.428	0.46	0.947	1495	347	0.427	0.47	0.941	1512
8	329	0.430	0.47	0.944	1335	328	0.428	0.46	0.947	1334	329	0.427	0.47	0.941	1335
9	326	0.430	1.00	0.650	467	326	0.428	1.00	0.650	616	327	0.427	1.00	0.650	629
10	315	0.430	1.00	0.650	467	315	0.428	1.00	0.650	467	316	0.427	1.00	0.650	476
11	289	0.430	1.00	0.650	-149	289	0.428	1.00	0.650	-140	289	0.427	1.00	0.650	-141
12	289	18.00	1.00	0.650	-135	289	18.00	1.00	0.650	-125	289	18.00	1.00	0.650	-125
13	323	18.00	1.00	0.650	24	323	18.00	1.00	0.650	24	324	18.00	1.00	0.650	28
14	783	18.00	1.00	0.650	2785	783	18.00	1.00	0.650	2818	783	18.00	1.00	0.650	2821
15	350	0.119	1.00	0.650	1805	350	0.122	1.00	0.650	1826	350	0.116	1.00	0.650	1822
16	346	0.119	1.00	0.650	1589	345	0.122	1.00	0.650	1594	347	0.116	1.00	0.650	1663
17	329	0.119	1.00	0.650	1056	329	0.122	1.00	0.650	1092	329	0.116	1.00	0.650	1079
18	319	0.119	1.00	0.650	881	321	0.122	1.00	0.650	927	320	0.116	1.00	0.650	909
19	308	0.119	3.55	0.388	164	308	0.122	3.44	0.395	182	309	0.116	3.40	0.394	196
20	289	0.119	3.55	0.388	-169	289	0.122	3.44	0.395	-169	289	0.116	3.40	0.394	-155
21	289	0.430	3.55	0.388	-168	289	0.428	3.44	0.395	-169	289	0.427	3.40	0.394	-154
22	325	0.430	3.55	0.388	-5	325	0.428	3.44	0.395	-1	326	0.427	3.40	0.394	7
23	325	0.430	0.53	0.388	-5	325	0.428	0.54	0.395	-1	326	0.427	0.53	0.394	7
24	325	0.430	3.02	0.388	-5	325	0.428	2.91	0.395	-1	326	0.427	2.87	0.394	7

^a The numbers refer to the stream numbers in Fig. 1.

^b T is the temperature, p is the pressure, m is the mass flow, w is the mass fraction of ammonia, and h is the enthalpy.

The thermal efficiency of the simulated cycle is dependent mostly on the enthalpy of the working fluid before and after the boiler and before and after the turbine, as well as on the mass flow ratio of the heat source gas and the working fluid. Before and after the boiler (the point after the boiler is the same point as the one before the turbine), the working fluid has the maximum pressure in the cycle and the differences between the correlations at high pressures could be expected to be of importance here.

If the pinch point in the boiler is located at the working fluid boiling point, the temperature and enthalpy of the working fluid bubble point influence the thermal efficiency, since they influence the gas flow/working fluid-ratio calculations. For low mass fractions of ammonia in the working mixture, the pinch point in the boiler is located at the working fluid boiling point. However, for higher mass fractions of ammonia for the working mixture, the mass flow ratio is dependent on the enthalpy of the working fluid before the boiler, since the pinch point in the boiler is then located here. Since the difference between the correlations is higher in the two-phase area, the difference in thermal efficiency in the cycle simulations is also higher for lower mass fractions of ammonia in the working mixture than for higher working mixture ammonia mass fractions.

When the maximum pressure in the power cycle is increased, the differences in enthalpy between the correlations are increased. This could be one reason why the differences in thermal efficiency increase with pressure, at least for the cases dependent on the bubble-point enthalpies.

7. CONCLUSIONS

The correlations for the properties of ammonia–water mixtures compared in this study give similar saturation properties at low temperature and pressures. The differences increase with temperature and pressure, and the largest differences occur for dew-point predictions. The new correlation presented by Tillner-Roth and Friend shows a slightly better agreement with experimental data and a more reasonable behavior when the critical point of the mixture is approached. Important differences between the correlations are that the correlations by Stecco and Desideri and by Ibrahim and Klein consider the vapor phase to be an ideal mixture, while the correlation by Tillner-Roth and Friend includes corrections for nonideal behavior for all phases. The Tillner-Roth and Friend correlation also includes data from a model concerning the vapor–liquid equilibrium behavior of mixtures in the critical region. Some differences in the predicted properties from the different correlations could also be due to different experimental data being used to derive the correlation.

When comparing the correlations in power cycle simulations, the difference in calculated thermal efficiency increases with the maximum pressure in the cycle. The cycle simulations performed in this study do not show larger differences in efficiency than about 4%, corresponding to about 1–1.5 percentage points. The difference in the working mixture mass fraction of ammonia giving the highest power cycle efficiency also increases with the maximum pressure in the cycle. It is as large as 0.10 for the highest pressure.

Even though the new correlation seems to be more theoretically reasonable than the correlations previously used in power cycle simulations, the differences in the final results of the thermal efficiency cycle simulations are still small. The conclusions made in earlier studies using the older correlations should therefore be reasonable. However, it should be pointed out that no, or very little, experimental data are available in the critical and supercritical region of the ammonia–water mixtures and that the behavior of the mixtures in this region is therefore uncertain.

ACKNOWLEDGMENTS

Thanks are due to Professor Gunnar Svedberg and Dr. Viktoria Martin at the Department of Chemical Engineering and Technology/Energy Processes, Royal Institute of Technology, for valued help with the work for this study. Part of this work was financed by the Swedish National Energy Administration (Statens Energimyndighet).

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