Entropy Generation Analysis of Heat Recovery Vapor Generator for Ammonia-Water Mixture

Chul Ho Han, Kyoung Hoon Kim

Abstract—This paper carries out a performance analysis based on the first and second laws of thermodynamics for heat recovery vapor generator (HRVG) of ammonia-water mixture when the heat source is low-temperature energy in the form of sensible heat. In the analysis, effects of the ammonia mass concentration and mass flow ratio of the binary mixture are investigated on the system performance including the effectiveness of heat transfer, entropy generation, and exergy efficiency. The results show that the ammonia concentration and the mass flow ratio of the mixture have significant effects on the system performance of HRVG.

Keywords—Entropy, exergy, ammonia-water mixture, heat exchanger.

I. INTRODUCTION

THERE is a strong need for the development of compact and low capacity systems to recover and upgrade waste heat streams to more usable forms, for over ninety percent of the world's primary energy utilization passes through a thermal transformation and much of the primary energy supply is ultimately rejected at low-grade waste heat [1]. When the source is low-temperature energy in the form of sensible heat, the thermal performance of power generation cycle using a pure substance becomes quite poor, because pure fluids have thermal properties of boiling and condensing at constant temperature under a constant pressure condition, which leads to large temperature differences in the vapor generator and condenser and, in turn, inevitably increases the irreversibilities in the system.

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 a proven technology for efficient utilizing of low-temperature heat sources [2], [3]. In the power generation system using ammonia-water mixture instead of pure working fluids, heat can be supplied or rejected at variable temperature but still at constant pressure, since the binary mixture evaporates over a wide range of temperature. The variable-temperature heat transfer process significantly alleviates the temperature mismatch between hot and cold streams in heat exchanging components of the system, which

C. H. Han is with Dept. Intelligent Mech. Eng., Kumoh National Institute of Technology, 61 Daehakro, Gumi, Gyeongbuk 730-701, Korea.

K. H. Kim is with Dept. Mech. Eng., Kumoh National Institute of Technology, 61 Daehakro, Gumi, Gyeongbuk 730-701, Korea (corresponding author, phone: 82-54-478-7292; fax: 82-54-478-7319; e-mail: khkim@kumoh.ac.kr).

This paper was supported by Research Fund, Kumoh National Institute of Technology.

then reduces the exergy destruction in the power cycles. In the past years the use of ammonia-water mixture as a working fluid in Rankine cycles has been investigated by many researchers for the purpose of reducing the thermal irreversibilities in the heat introduction process, particularly between the heat source and the evaporating working fluid [4]-[11].

As the thermodynamic analysis based on the first law has inherent limitations of no distinction between work and heat and no provision of quantifying the quality of heat, the method of entropy and exergy analysis based on the second law is well suited for furthering the goal of more effective energy resources use, for it enables the location, cause, and true magnitude of waste and lost to be determined [12], [13] and may give much more meaningful evaluation by indicating the association of irreversibilities of the system [14], [15].

When heat is transferred in a heat exchanger, the degradation of energy occurs due to irreversibility, but the first law of thermodynamics just deals with the quantity of energy and cannot evaluate the quality of energy. However, the second law of thermodynamics deals with quantifying the quality of energy, so it is proper for evaluating performances of heat exchanger system and heat transfer intensification techniques. It shows that not all the energy input into a system can be used effectively and the irreversibility of the heat exchange process could be characterized by the increase of entropy generation [16]-[20].

Kim et al. [21]-[24] investigated the thermodynamic performances of ammonia-water based power generation cycles for the recovery of low-temperature heat sources and showed that the characteristics of temperature distributions in the fluid streams of the heat exchangers vary quite complicatedly and sensitively with changing system parameters. They also presented the first and second thermodynamic law analysis for heat recovery vapor generator (HRVG) of ammonia-water mixture when the heat source is low-temperature energy in the form of sensible heat [25]. In the present work, thermodynamic analysis of entropy and exergy is performed for HRVG of ammonia-water mixture to covert low-temperature heat source to useful form of energy. The HRVG consists of pre-heater, evaporator and superheater, and the heat source is in the form of sensible energy. Special attention is focused on the effects of the mass flow ratio and the ammonia mass concentration of the working fluid on the thermodynamic performance of HRVG.

II. SYSTEM ANALYSIS

The schematic diagram of HRVG is shown in Fig. 1. The

source fluid enters HRVG with thermal capacity C_s and temperature T_s, where thermal capacity is product of mass flow rate ms and isobaric specific heat c_{ps} of source fluid. On the other hand, ammonia-water mixture enters HRVG with mass flow rate m, temperature T_{in}, pressure P, and ammonia mass concentration x_b, is heated by the hot source stream, and then leaves HRVG with temperature T_{out}.
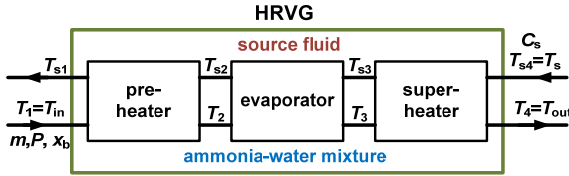

Fig. 1 Schematic diagram of HRVG

The important assumptions in the present cycle analysis are as follows [25]: 1) The fluid flow and heat transfer rates are steady. 2) Heat loss between the system and environment is negligible so that heat transfer occurs only between hot and cold fluid streams in the heat exchangers. 3) Pressure drop due to flows inside heat exchangers is negligible so that the pressure inside a heat exchanger is maintained constant. 4) The kinetic energy and the potential energy changes of the fluids in and out of the heat exchangers are negligible. 5) The longitudinal heat conduction in the tube walls is negligible.

Let us denote that the mass flow rate m, ammonia mass concentration x_b, and inlet and outlet temperatures T_{in} (= T_1) and T_{out} (= T_4) of the ammonia-water mixture, and the thermal capacity C_s and inlet temperature T_s (= T_{s4}) of source fluid are specified. Then, the source-fluid temperatures T_{s1}, T_{s2} and T_{s3} can be obtained from the energy balance equations in HRVG [25]:

$$Q_{ph} = m(h_2 - h_1) = C_s(T_{s2} - T_{s1}) \qquad (1)$$

$$Q_{ev} = m(h_3 - h_2) = C_s(T_{s3} - T_{s2}) \qquad (2)$$

$$Q_{sh} = m(h_4 - h_3) = C_s(T_{s4} - T_{s3}) \qquad (3)$$

$$Q_{tot} = m(h_4 - h_1) = C_s(T_{s4} - T_{s1}) \qquad (4)$$

where h is the specific enthalpy of the mixture, Q is the heat transfer rate of a heat exchanger, and the subscripts of ph, ev, sh, and tot indicate pre-heater, evaporator, superheater, and total system of HRVG, respectively. Note that h_2 and h_3 are specific enthalpies at the bubble and dew points of the mixture, respectively, for the prescribed conditions of pressure P and ammonia mass concentration x_b.

The entropy generations, which are equal to the difference of entropy outflow from the system and entropy inflow to the system, can be obtained as follows:

$$\Delta S_{ph} = m(s_2 - s_1) - C_s \ln(T_{s2} / T_{s1}) \qquad (5)$$

$$\Delta S_{ev} = m(s_3 - s_2) - C_s \ln(T_{s3} / T_{s2}) \qquad (6)$$

$$\Delta S_{sh} = m(s_4 - s_3) - C_s \ln(T_{s4} / T_{s3}) \qquad (7)$$

$$\Delta S_{tot} = m(s_4 - s_1) - C_s \ln(T_{s4} / T_{s1}) \qquad (8)$$

where s is the specific entropy of the mixture.

The exergy efficiency (exergy recovery index or second law efficiency) of a heat exchanger η may be defined as the ratio of the increased exergy of cold stream to the decreased exergy of hot stream [12], [18]. Then, the exergy efficiency of each heat exchanger in HRVG can be obtained as follows [25]:

$$\eta_{ph} = \frac{m}{C_s} \frac{(h_2 - h_1) - T_0(s_2 - s_1)}{(T_{s2} - T_{s1}) - T_0 \ln(T_{s2} / T_{s1})} \qquad (9)$$

$$\eta_{ev} = \frac{m}{C_s} \frac{(h_3 - h_2) - T_0(s_3 - s_2)}{(T_{s3} - T_{s2}) - T_0 \ln(T_{s3} / T_{s2})} \qquad (10)$$

$$\eta_{sh} = \frac{m}{C_s} \frac{(h_4 - h_3) - T_0(s_4 - s_3)}{(T_{s4} - T_{s3}) - T_0 \ln(T_{s4} / T_{s3})} \qquad (11)$$

$$\eta_{tot} = \frac{m}{C_s} \frac{(h_4 - h_1) - T_0(s_4 - s_1)}{(T_{s4} - T_{s1}) - T_0 \ln(T_{s4} / T_{s1})} = \frac{\Delta E_w}{\Delta E_s} = 1 - \frac{T_0 \Delta S_{tot}}{\Delta E_s} \qquad (12)$$

where the subscript 0 indicates the dead state.

In this work, thermodynamic properties of liquid and vapor phases of the ammonia-water mixture are evaluated by using the excess Gibbs free energy [26] and the equilibrium states of liquid and vapor phases are calculated using the methods presented in [21].

III. RESULTS AND DISCUSSIONS

In the present study, thermodynamic analysis of the HRVG of ammonia-water mixture is carried out. The basic data of the system variables are as follows: T_s = 200°C, T_{in} = 30°C, T_{out} = 190°C, T_0 = 298.15 K, C_s = 10 kW/K, P = 15 bar. The key parameters in this study are the ammonia mass concentration and the mass flow ratio which is defined as the ratio of mass flow rate of ammonia-water mixture to the source fluid.

The effectiveness of heat exchanger ε is defined as the ratio between actual heat transfer rate and the maximum possible heat transfer rate and it can be approximately obtained as follows:

$$\varepsilon = \frac{T_s - T_{s1}}{T_s - T_{in}} \qquad (13)$$

The effectiveness of HRVG is plotted against the ammonia mass concentration in Fig. 2 for various mass flow ratios. It can be seen from the figure that the effectiveness generally decreases with increasing ammonia mass concentration, because the vaporization heat of ammonia-water mixture decreases with increasing ammonia mass concentration. For a specified ammonia mass concentration, the effectiveness

becomes higher as the mass flow ratio increases, since a high mass flow rate of the working fluid results in a high heat transfer in the heat exchanger and consequently a high effectiveness of HRVG.
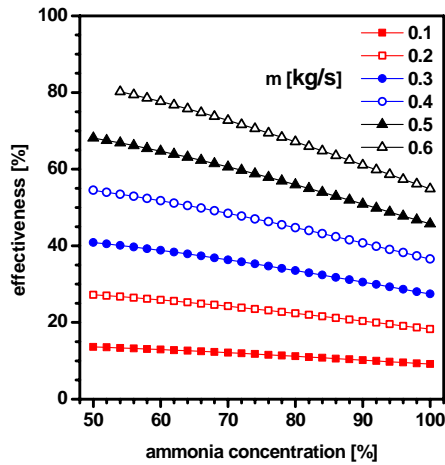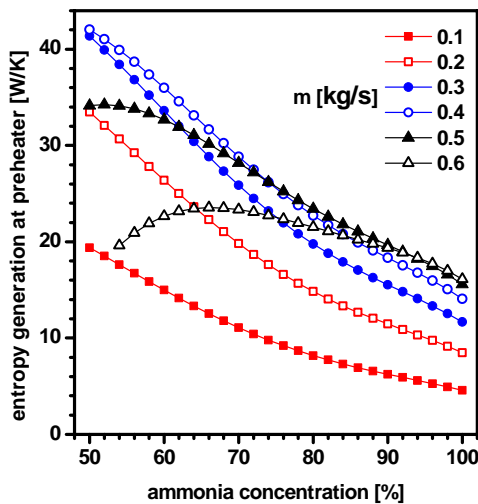

Fig. 2 Effectiveness of HRVG

Fig. 3 Entropy generation of preheater

As aforementioned, the entropy generation is a measure of the irreversibility in heat exchangers and can be obtained from (5)-(8) for preheater, evaporator, superheater, and HRVG. HRVG is consisted of preheater, evaporator, and superheater. Fig. 3 shows the entropy generation at the preheater as a function of ammonia mass concentration for various mass flow ratios. The entropy generation in the preheater shows a decreasing tendency with respect to the ammonia concentration for low mass flow ratios. When the mass flow ratio is high, for example 0.6, however, the entropy generation increases firstly with increasing ammonia mass concentration and reaches a peak value and then decreases again. This can be explained as follows. The entropy generation at preheater ΔS_{ph} can be obtained by subtracting the entropy decrease in source fluid

$\Delta S_{s,ph} = C_s(T_{s2}-T_{s1})$ from the entropy increase in the ammonia-water mixture $\Delta S_{w,ph} = m(h_2-h_1)$ as (5). As the ammonia mass concentration increases, each of $\Delta S_{w,ph}$ and $\Delta S_{s,ph}$ decreases, but the decreasing rate of $\Delta S_{s,ph}$ is greater than that of $\Delta S_{w,ph}$. For a specified ammonia mass concentration, the entropy generation has a peak with respect to the mass flow rate, because $\Delta S_{w,ph}$ increases proportional to the mass flow ratio.
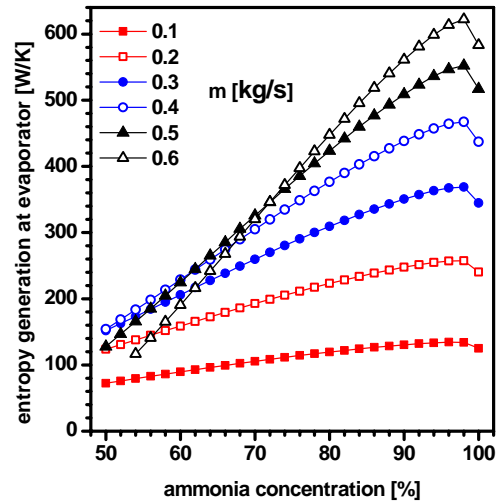

Fig. 4 Entropy generation of evaporator

The entropy generation at evaporator is plotted in Fig. 4 as a function of ammonia mass concentration for various mass flow ratios. For a given mass flow ratio, the entropy generation increases generally with increasing ammonia mass concentration except for very high mass concentrations, which is mainly due to the increased temperature difference between the hot and cold streams in the heat exchanger as ammonia mass concentration increases. The entropy generation and its increasing rate generally increase with increasing mass flow ratio.
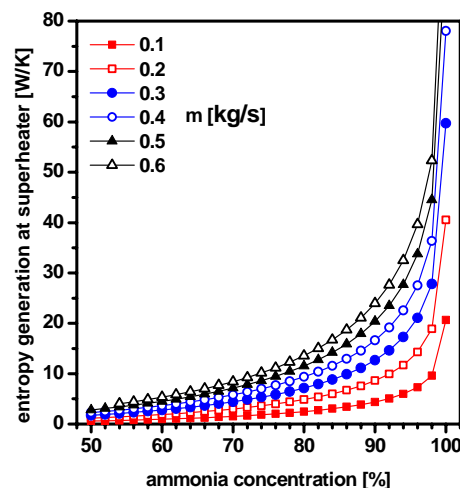

Fig. 5 Entropy generation of superheater

The entropy generation in the superheater is plotted in Fig. 5 against ammonia mass concentration for various mass flow ratios. For a given mass flow ratio, the entropy generation increases with increasing ammonia mass concentration, due to the increased temperature difference between the streams with increasing ammonia mass concentration. For a specified ammonia mass concentration, the entropy generation increases, as the mass flow ratio increases.
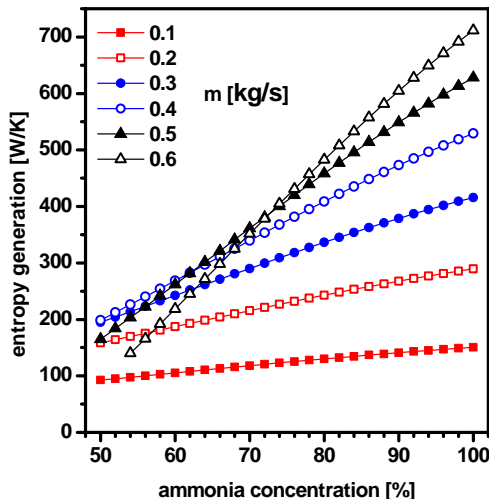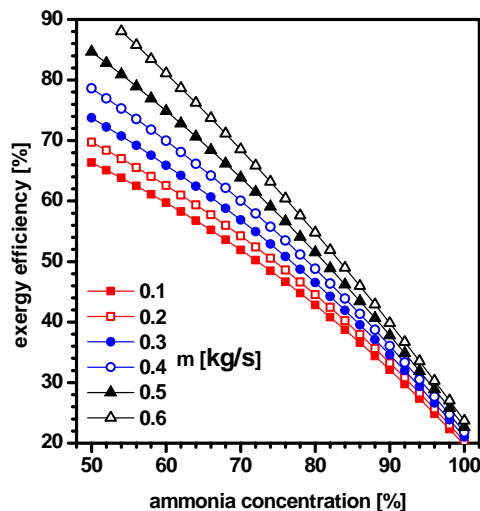

Fig. 6 Entropy generation of HRVG

Fig. 7 Exergy efficiency of HRVG

Fig. 6 illustrates the effects of ammonia mass concentration and mass flow ratio of working fluid on the entropy generation of total HRVG system. The entropy generation increases with increasing ammonia mass concentration, which is similar to that for the evaporator because the portion of heat transfer at evaporator is dominant in the HRVG. The increasing rate of the entropy generation of HRVG increases with increasing mass flow ratio. Therefore, for low ammonia mass concentration, the entropy generation can have a peak value with respect to the mass flow ratio.

Fig. 7 shows the exergy efficiency of HRVG for various ammonia mass concentration and mass flow ratios. It can be seen from the figure that the exergy efficiency decreases with increasing ammonia mass concentration or decreasing mass flow ratio, which is due to increased temperature difference between the hot and cold streams and the consequent increased entropy generation in HRVG.

IV. Conclusion

A performance analysis is carried out based on the first and second laws of thermodynamics for the heat recovery vapor generator (HRVG) of ammonia-water mixture. HRVG consists of preheater, evaporator, and superheater and the heat source is low-temperature heat source in the form of sensible energy. The ammonia mass concentration and mass flow ratio of the working fluid are considered as the key parameters. The results show that the ammonia mass concentration and the mass flow ratio exhibit significant effects on the system performance such as the effectiveness of heat exchanger, entropy generation and exergy efficiency. In general, the entropy generation increases but the exergy efficiency decreases with increasing ammonia concentration. However, the entropy generation can possess a local maximum value with respect to the mass flow ratio of working fluid for low ammonia mass concentration.

References

[1] A. B. Little and S. Garimella, "Comparative assessment of alternative cycles for waste heat recovery and upgrade," *Energy*, vol. 36, pp. 4492-4504, 2011.
[2] C. Zamfirescu and I. Dincer, "Thermodynamic analysis of a novel ammonia–water trilateral Rankine cycle," *Thermochimica Acta*, vol. 477, pp. 7-15, 2008.
[3] A. Khaliq, "Exergy analysis of gas turbine trigeneration system for combined production of power and heat and refrigeration," *Int. J. Refrig.*, vol. 32, pp. 534-545, 2009.
[4] O. M. Ibrahim, "Design consideration for ammonia–water Rankine cycle," *Energy*, vol. 21, pp. 835-841, 1996.
[5] M. Jonsson and J. Yan, "Ammonia–water bottoming cycles: a comparison between gas engines and gas diesel engines as prime movers," *Energy*, vol. 26, pp. 31-44, 2001.
[6] V. A. Prisyazhniuk, "Alternative trends in development of thermal power plant," *Appl. Therm. Eng.*, vol. 28, pp. 190-194, 2008.
[7] N. Kiani, A. Akisawa, and T. Kashiwagi, "Thermodynamic analysis of loadleveling hyper energy converting and utilization system," *Energy*, vol. 33, pp. 400-409, 2008.
[8] P. Roy, M. Désilets, N. Galanis, H. Nesreddine, and E. Cayer, "Thermodynamic analysis of a power cycle using a low-temperature source and a binary NH3-H2O mixture as working fluid," *Int. J. Therm. Sci.*, vol. 49, pp. 48-58, 2010.
[9] P. Bombarda, C. M. Invernizzi, and C. Pietra, "Heat recovery from Diesel engines: A thermodynamic comparison between Kalina and ORC cycles," *App. Therm. Eng.*, vol. 30, pp. 212-219, 2010.
[10] X. Shi and D. Che, "A combined power cycle utilizing low-temperature waste heat and LNG cold energy," *Energy*, vol. 50, pp. 567-575, 2009.
[11] J. Wang, Z. Yan, and M. Wang, "Thermodynamic analysis and optimization of an ammonia-water power system with LNG (liquefied natural gas) as its heat sink," *Energy*, vol. 50, pp. 513-522, 2013.
[12] A. Bejan, *Advanced Engineering Thermodynamics*, 3rd ed., John Wiley & Sons, New York. NY, USA, 2006.
[13] A. Bejan, G. Tsatsaronis, and M. Moran, *Thermal Design and Optimization*, John Wiley & Sons, New York, NY, USA, 1996.
[14] N. Lior and N. Zhang, "Energy, exergy, and second law performance criteria," *Energy*, vol. 32, pp. 281-296, 2007.

[15] D. Tarlet, Y. Fan, S. Roux, and L. Luo, "Entropy generation analysis of a mini heat exchanger for heat transfer intensification," *Exp. Therm. Fluid Sci.*, in press, 2013.

[16] E. A. Sciubba, "A minimum entropy generation procedure for the discrete pseudo-optimization of finned-tube heat exchangers," *Rev. Gen. Therm.*, vol. 35, pp. 517-525, 1996.

[17] P. Naphon, "Second law analysis on the heat transfer of the horizontal concentric tube heat exchanger," *Int. Commun. Heat Mass*, vol. 33, pp. 1029-1041, 2006.

[18] J. Y. San, "Second-law performance of heat exchangers for waste heat recovery," *Energy,* vol. 35, pp. 1936-1945, 2010.

[19] B. David, J. Ramousse, and L. Luo, "Optimization of thermoelectric heat pumps by operating condition management and heat exchanger design," *Energ. Convers. Manage.*, vol. 60, pp. 125-133, 2012.

[20] G. Giangaspero and E. Sciubba, "Application of the entropy generation minimization method to a solar heat exchanger: A pseudo-optimization design process based on the analysis of the local entropy generation maps," *Energy*, vol. 58, pp. 52-65, 2013.

[21] K. H. Kim, C. H. Han and K. Kim, "Effects of ammonia concentration on the thermodynamic performances of ammonia-water based power cycles," *Thermochimica Acta*, vol. 530, pp. 7-16, 2012.

[22] K. H. Kim, C. H. Han, and K. Kim, "Comparative exergy analysis of ammonia-water based Rankine cycles with and without regeneration," *Int. J. Exergy*, vol. 12, pp. 344-361,2013

[23] K. H. Kim and K. C. Kim, "Thermodynamic performance analysis of a combined power cycle using low grade heat source and LNG cold energy," *App. Therm. Eng.*, in press, 2014.

[24] K. H. Kim, H. J. Ko, and K. Kim, "Assessment of pinch point characteristics in heat exchangers and condensers of ammonia–water based power cycles, *Appl. Energy*, vol. 113, pp. 970-981, 2014.

[25] K. H. Kim, K. Kim, and H. J. Ko, "Entropy and exergy analysis of a heat recovery vapor generator for ammonia-water mixtures," *Entropy*, vol. 16, pp. 2056-2070, 2014.

[26] F. Xu and D. Y. Goswami, "Thermodynamic properties of ammonia–water mixtures for power-cycle application," *Energy*, vol. 24, pp. 525-536, 1999.