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Second Law Analysis of Ammonia-Water Power Cycle for Direct-Fired Cogeneration Application[*]

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Abstract

Exergy analysis is performed for four biomass-fueled power cycles presented in a previous study, (Dejfors et al. 1997). Ammonia-water power cycles are compared with Rankine steam cycles for both direct-fired cogeneration application and conventional condensing power application. For all applications studied, the ammonia-water cycle has less exergy losses in the condensers but higher exergy losses in the boiler and in the internal heat exchange system compared with the Rankine cycle. In the condensing case, the superior heat exchange in the condenser for the ammonia-water cycle counterbalances the inferior heat exchange in the internal heat exchangers and in the boiler. In the cogeneration case, the useful exergy out from the turbines and to the district heating network is higher for the Rankine cycle.

Key words: *cogeneration, exergy analysis, ammonia, water, binary mixtures, biomass*

1. Introduction

In Sweden, most of the new power plants being built are biomass-fueled cogeneration plants. They generate power and produce heat for district heating. The Swedish Parliament has set objectives for carbon dioxide emissions which mean that, by the year 2000, emission levels shall not exceed those of 1990, and they shall thereafter be further reduced (Energy in Sweden 1995). Vast land areas in Sweden are covered with forests. Since biomass does not contribute to the global sum of carbon dioxide and has a low content of sulfur, it is a very interesting fuel. Swedish biomass-based cogeneration plants are quite small, often less than 100 MW_{fuel}.

In a previous study (Dejfors et al. 1997), ammonia-water power cycles were compared with Rankine steam cycles for direct-fired cogeneration applications. A conventional condensing power application was also studied. The result for the cogeneration case was that a simple ammonia-water cycle has a lower net power efficiency than a Rankine steam cycle. For the condensing application, the ammonia-water cycle has a slightly higher net power efficiency.

The aim of the study reported here was to perform exergy analysis of the different applications. An evaluation of the results and a discussion on possible improvements to be made on the existing ammonia-water process for the cogeneration case are also included.

2. Theory on Ammonia-Water Cycles

A two-component mixture may have some thermodynamic advantages compared with a one component fluid. At a constant pressure, a two-component mixture boils with an increasing temperature and it condenses with a decreasing temperature. This makes it possible to better adjust the temperature profile to the heat source and the heat sink, if the heat source has a decreasing temperature and the heat sink has an increasing temperature. The ammonia-water mixture is the best known mixture used in power cycles. It is a non-azeotropic mixture. The most famous ammonia-water mixture cycle is the Kalina cycle (generic term for all ammonia-water cycles presented by Dr. A. Kalina). Many investigations have been published which show the advantages of the Kalina cycle, for example as a bottoming cycle (Olsson et al. 1994), a geothermal cycle (Lazzeri et al. 1995) and a direct-fired cycle (Kalina 1991).

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3. Systems and Assumptions

Four systems from (Dejfors et al. 1997) are studied in this paper, two cogeneration configurations and two normal condensing configurations. The ammonia-water cycle and the Rankine steam cycle in the cogeneration case are shown in *Figures 1* and *2* respectively. The district heating network has a return temperature of 50ºC and a supply temperature of 100ºC. Stream data for the cycles are shown in the figures.

The cogeneration ammonia-water cycle has ÿÿo sunerheaamÿÿ (SH1, SH2) situated outside tÿÿÿÿoiappl In these, the vapor is heated by the exhaust stream from the high pressure and low pressure turbine respectively. A partly condensed stream goes into the separator and out from the separator (SEP) there are two streams, one with a low ammonia fraction and one with a high ammonia fraction. The stream with the low ammonia fraction is used to lower the ammonia fraction in the hot stream before preheater 3 (PH3) and preheater 2 (PH2). This provides a better heat exchange. After that, the composition is restored in the mixing point 4 (mix4) and then the stream is condensed in the district heating condenser (COND).

The cogeneration Rankine steam cycle is similar to an existing direct-fired biomass-fueled cogeneration plant in Enköping, Sweden. The cycle has three extraction streams from the tur-

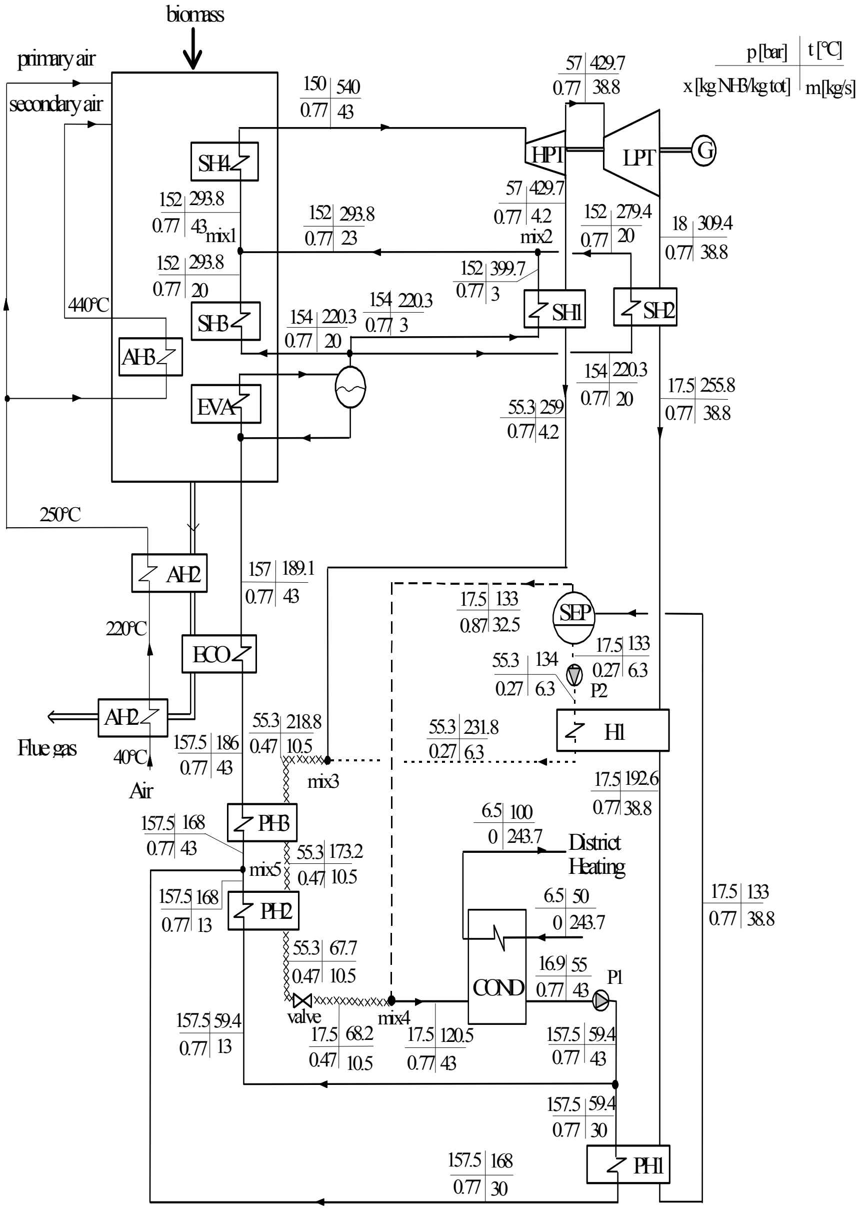

Figure 1. Cogeneration ammonia-water cycle.

bines to the preheating process. The fourth extraction stream and the exhaust stream from the low pressure turbine are condensed in two district heating condensers.

The two condensing configurations are based on the above cogeneration designs in order to achieve as plain a comparison as possible. The only thing that differs from the ammonia-water application in *Figure 1* is that there is no superheater (SH2) after the low-pressure turbine in the condensing case. For the Rankine steam cycle, the second condenser (COND2) in *Figure 2* is replaced by a preheater. Thus the last extraction stream from the low-pressure turbine exchanges heat in a preheater. The cooling water has an inlet temperature of 10ºC and outlet temperature of 25ºC.

Process data were calculated using the simulation program IPSEpro. IPSEpro is an equation-solving program from SimTech Simulation Technology (IPSEpro). The thermodynamic properties of ammonia-water mixtures were obtained by using a library of subroutines developed by Stecco and Desideri (1989). The subroutines were developed for pressures up to 115 bar. To be able to use the subroutines in this study, the functions have been extrapolated to higher pressures. An interface has been implemented between IPSEpro and the thermodynamic subroutines.

Parameters used in the calculations are shown in TABLE I. The flue gas properties, enthalpy, entropy and temperature, are calculated by using polynomials found in literature (Rivkin 1988). The adiabatic temperature of combustion is calculated and the flue gas temperature decreases during heat exchange in the superheaters, evaporator, economizer and several air preheaters. The air is preheated in three heat exchangers. In the first and second air preheater (AH1, AH2), the air is heated from around 40°C to 250°C. 30% of the air mass flow is then heated to 440°C before it enters the boiler. The flue gas has a temperature of 143°C after air preheater 1 (AH1). The outdoor temperature of the air is set to 0°C. The combustion efficiency is 100%. Energy losses due to radiation in the boiler are set to 1.8% of the fuel input. The air and the flue gas are assumed to have the environmental reference pressure.

4. Exergy Calculations

There are several ways to evaluate a cycle configuration from a thermodynamic point of view. The amount of energy in different parts of the cycle is calculated by first law analysis. Another way is to study how the energy quality changes through the cycle. The term exergy describes the maximal amount of work that can be extracted from a stream as it passes to the state of the environment.

TABLE I. Parameters Used in Calculations.

Biomass	fuel composition	$x_C = 0.2499$	$x_{N2}=0.0020$	$x_{H2O}=0.5100$
	[mass fraction]	$x_{H2} = 0.0304$	$x_{O2}=0.1980$	$x_{ash}=0.0098$
	Lower Heating Value [MJ/kg]	LHV = 8.43		
	fuel input [MW]	82.2		
Power cycles	excess air factor	1.3	Isentropic efficiency	
	boiler efficiency	0.91	turbine	0.88
	minimum vapor quality		pump	0.80
	of turbine exhaust	0.9		
	mechanical and generator efficiency	0.98	Pressure losses	
			condenser	5%
	minimum temperature difference		boiler	3%
	vapor - vapor	30°C	reheat	3%
	vapor - liquid	15°C	hot side of external	
	liquid - liquid	5°C	superheater	3%
	boiling - condensation	5°C		
Environment state	air composition	$\bar{x}_{O2} = 0.2091$	$\bar{x}_{H2O}=0.0037$	$\bar{x}_{CO2}=0.0002$
	[molar fraction]	$\bar{x}_{N2} = 0.7776$	$\bar{x}_{Ar}=0.0094$	
	reference temperature [ºC]	$t_{ref}= 0$		
	reference pressure [bar]	$p_{ref}= 1.013$		
	relative humidity of air [%]	60		

Reference state for water and ammonia-water calculations	reference temperature [°C]	$t_{ref} = 15$
	reference pressure [bar]	$p_{ref} = 1.013$
	ammonia concentration [mass fraction]	$x_{NH3} = 0.99$

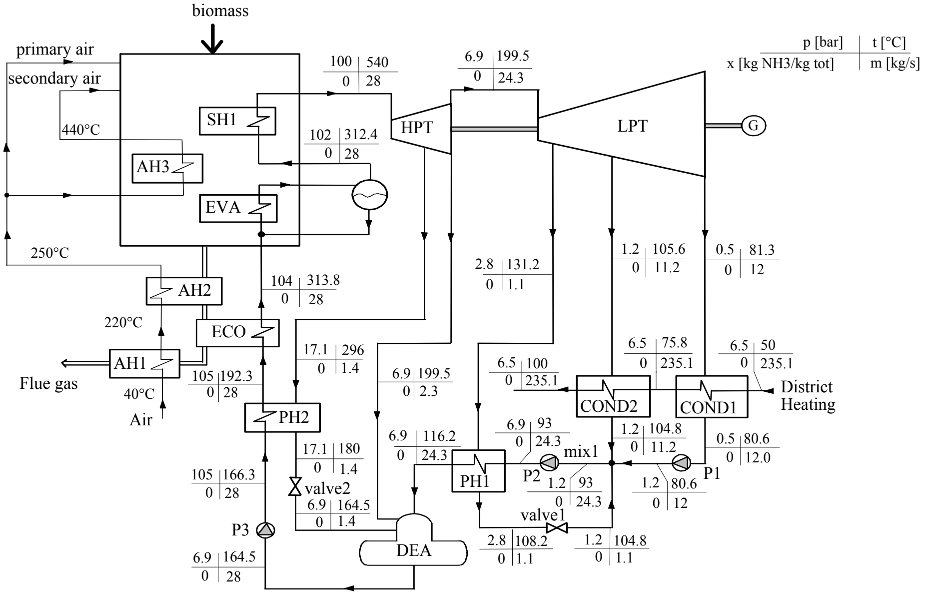

Figure 2. Cogeneration Rankine steam cycle.

The fuel exergy consists of the chemical and physical exergy. The physical exergy has not been taken into account here. The chemical exergy of the biomass is as stated below (Szargut et al. 1988).

$$e_{ch,f} = \beta(LHV + h_{vap} x_{H2O}) + e_{ch,H2O}\, x_{H2O} \quad (1)$$

where $\beta = \beta_1 / \beta_2$ (2)

$$\beta_1 = 1.0412 + 0.2160(x_H/x_C) + 0.0450(x_N/x_C) - 0.2499(x_O/x_C)[1 + 0.7884(x_H/x_C)] \quad (3)$$

$$\beta_1 = (1 - 0.3035)(x_O/x_C) \quad (4)$$

where x_H, x_O, x_N, x_C are the weight percent of H_2, O_2, N_2 and C respectively in the fuel.

The chemical exergy of the fuel is the sum of the chemical exergy for the combustible substances and the chemical exergy of the liquid water, equation 1. The chemical exergy in the ash is neglected. The lower heating value of the moist fuel, LHV, is 8.43 MJ/kg. The heat of vaporization, h_{vap}, is 2.44 kJ/kg. The chemical exergy of liquid water is taken from a diagram in (Szargut et al. 1988), $e_{ch,H2O}$=64 kJ/kg. The above data result in a specific fuel exergy of 10.87 MJ/kg. The fuel exergy is then 105.98 MW.

The reference state for water and ammonia-water calculations is given in TABLE I. Note that the reference temperature for the working fluid and cooling water (t_{ref}=15 °C) is different from the reference temperature for the air and flue gas (t_{ref}=0 C). However, when calculating the exergy decrease and increase over cycle components the reference temperature has no influence since it cancels out.

The exergy in water and ammonia-water streams is calculated from

$$E_{st} = m_{st}[(h(T) - h(T_{ref}) - T_{ref}(s(T) - s(T_{ref})] \quad (5)$$

The flue gas and the air are assumed to be ideal gas mixtures. Equation (5), in molar basis, is for the flue gas and air, written as follows, where n is the number of compounds in the gas

$$E_g = \bar{m}_g \sum_{k=1}^{n} x_k \{\bar{h}_k(T) - \bar{h}_k(T_{ref}) - T_{ref}[\bar{s}_k(T) - \bar{s}_k(T_{ref}) - \bar{R}T_{ref}\ln(\frac{\bar{x}_k p}{\bar{x}_k p_{ref}})]\} \quad (6)$$

Stream data for ammonia-water and water properties are calculated using IPSEpro. The air and flue gas properties are calculated in EES, Engineering Equation Solver, by F-Chart Software (EES). Relevant data are then transferred to the spreadsheet program Microsoft EXCEL. All exergy calculations are performed in EXCEL.

The second law efficiency, ε, for the net power production and the district heat production is described as the ratio

$$\varepsilon = \frac{\text{exergy out in product}}{\text{exergy in}} = \quad (7)$$

$$= \frac{\text{net power output+exergy increase in DH network}}{\text{fuel exergy}}$$

Here, it is assumed that the air is taken from the same enclosed space where the boiler is placed and thus is at a higher temperature (40 °C) than the reference temperature (0 °C). Nevertheless, the exergy content of the inlet air is assumed negligible as compared to the fuel exergy content.

In the condensing applications the only exergy out in product is the net power.

5. Results and Discussion

The exergy in all process streams has been calculated. With an exergy analysis it is possible to examine how well the cycle is using the exergy supplied to the system. Table II and Table III show the exergy destruction for each component for the ammonia-water cogeneration cycle and the cogeneration Rankine steam cycle respectively.

The combustion exergy destruction is calculated as the difference between the fuel exergy plus the exergy in the air entering the boiler and the exergy in the flue gas from adiabatic combustion. The fuel exergy is 105.98 MW.

The losses due to radiation are assumed to occur directly after the flue gas has reached the adiabatic temperature of combustion. The exergy loss for the economizer in the Rankine steam cycle is higher than in the ammonia-water cycle. This is due to the fact that the working fluid in the Rankine steam cycle has a higher boiling temperature and needs more heat in the economizer. Instead, the ammonia-water cycle needs more energy to superheat its working fluid and therefore it has a higher exergy loss in the superheaters.

TABLE II. Cogeneration Ammonia-Water Cycle.

	Exergy losses	Exergy losses in percent of fuel exergy
	[kW]	[%]
AH1+AH2+AH3	2337.34	2.21
ECO	680.18	0.64
EVA	9092.00	8.58
SH1	93.08	0.09
SH2	371.29	0.35
SH3	2316.57	2.19
SH4	9751.20	9.20
HPT	972.94	0.92
LPT	1033.19	0.97
COND	433.82	0.41
H1	183.35	0.17
PH1	1070.13	1.01
PH2	259.60	0.24
PH3	126.51	0.12
mix1+mix2	52.82	0.05
mix3+mix4+mix5	370.29	0.35
P1+P2	224.57	0.21
valve1	42.04	0.04
SEP	0.88	0.00
Radiation	1199.49	1.13
Exhaust gas	8989.47	8.48
Combustion	34892.73	32.92

A compact version of the exergy losses for the four cycles is shown in TABLE IV. One third of the fuel exergy is lost during combustion. Another big part of the exergy is lost in the boiler. The adiabatic temperature of combustion is around 1460°C and the highest temperature of the working fluid is 540°C. This results in a high temperature difference in most parts of the boiler.

For both applications, the ammonia-water cycle shows no thermodynamic advantages in the boiler. In the boiler the dew point for ammonia-water is almost 100°C lower than the bubble point for water. The ammonia-water cycles have better heat exchange in the condensers compared with the Rankine steam cycles. The temperature of the condensing fluid decreases, which results in a better matching of the temperature. However, the internal heat exchange (includes preheaters, mixing points, pumps, valves and superheaters after turbines) shows a lower exergy destruction for the Rankine steam cycle.

TABLE III. Cogeneration Rankine steam cycle.

	Exergy losses	Exergy losses in percent of fuel exergy
	[kW]	[%]
AH1+AH2+AH3	2562.56	2.42
ECO	3691.77	3.48
EVA	10447.16	9.86
SH1	6038.41	5.70
HPT	1646.95	1.55
LPT	977.74	0.92
COND1	1143.96	1.08
COND2	902.42	0.85
PH1	117.17	0.11
PH2	121.34	0.11
DEA	201.54	0.19
mix1	16.19	0.02
P1+P2+P3	162.90	0.15
valve1+valve2	2.33	0.00
Radiation	1199.49	1.13
Exhaust gas	8988.99	8.48
Combustion	34892.73	32.92

For the two cogeneration configurations, following the fuel through the process to the exhaust gas, 93% of the exergy loss takes place in the combustion and heat exchange in the boiler. For the condensing cases, 87-88% of the exergy loss takes place in the boiler.

TABLE V shows the useful exergy out from the cycles. The two cogeneration configurations have previously been optimized to achieve the highest possible net power output (Dejfors et al. 1997). The difference in net power is 1.6%, but for the second law efficiency, ε, the difference is 1.3%. This is due to that the ammonia-water cycle produces a higher mass flow in the district heating network.

TABLE IV. Exergy Losses in Different Parts of the Cycle for the Different Cycle Configurations.

	Exergy losses in percent of fuel exergy							
	Combustion	Heat exchange between flue gas and working fluid	Heat exchange between flue gas and air	Radiation and exhaust gas	Turbine	Condenser	Internal heat exchange	Sum
Cogeneration ammonia-water cycle	32.9	20.6	2.2	9.6	1.9	0.4	2.6	70.2
Cogeneration Rankine steam cycle	32.9	19.0	2.4	9.6	2.5	1.9	0.6	68.9
Condensing ammonia-water cycle	32.9	20.8	2.2	9.6	2.6	2.7	3.5	74.3
Condensing Rankine steam cycle	32.9	19.0	2.4	9.6	2.8	7.3	0.7	74.7

In the condensing application, the ammonia-water cycle has a great advantage in the condenser. The Rankine steam cycle is hampered by the vapor quality condition. The condensing power configurations are based on the cogeneration designs, in order to achieve as good a comparison as possible. This implies that the ammonia-water condensing cycle is probably not well designed.

The improvements to be made on the ammonia-water cogeneration cycle should be in the heat exchange with the flue gas and in the internal heat exchange system. Improvements of the internal heat exchange network would probably result in more separators, streams with different ammonia concentrations, mixing points and heat exchangers. For the cogeneration application the gain for the development is a very small part of the total exergy loss (around 2%).

TABLE V. Useful Exergy Output from the Different Cycle Configurations

	Exergy Out in Product In Precent of Fuel Exergy		
	Net Power	District Heating	ε
Cogeneration ammonia-water cycle	21.5	8.3	29.8
Cogeneration Rankine steam cycle	23.1	8.0	31.1
Condensing ammonia-water cycle	25.7		25.7
Condensing Rankine steam cycle	25.2		25.2

To improve the heat exchange in the boiler a higher maximum pressure in the cycle is probably needed. Since no correlations for the thermodynamic properties of the ammonia-water mixture at high pressures and temperatures are available today, it was not possible to perform simulations at higher pressures.

6. Conclusions

The exergy analysis shows that most of the exergy destruction takes place in the boiler. About 87 to 93% of the total exergy loss takes place during combustion and heat exchange in the boiler. The ammonia-water cycles have lower exergy losses in the condensers but higher exergy losses in the boiler and in the internal heat exchange system compared with the Rankine steam cycles. In the boiler the dew point for ammonia-water is almost 100°C lower than the bubble point of water. A large part of the boiling process takes place in the boiler. The temperature profile of the working fluid is closer to the profile of flue gas for the Rankine steam cycle than for the ammonia-water cycle in the direct-fired application investigated in this paper. The useful exergy is higher in the cogeneration application of the Rankine steam cycle. In the condensing application the ammonia-water cycle has a slightly higher net power output and consequently a lower total exergy loss.

The two most feasible alternatives to improve the ammonia-water cogeneration cycle are reducing the exergy loss in the internal heat exchange system or in the boiler. The first alternative would complicate the system with limited gain and the second alternative needs more reliable thermodynamic properties at high pressure and temperatures to be developed.

Acknowledgement

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Nomenclature

DH	District Heating	
E	Exergy flow rate	[kW]
e	Specific exergy	[kJ/kg]
h	Enthalpy	[kJ/kg]
$\bar{h}$	Enthalpy	[kJ/kmole]
h_{vap}	Heat of vaporization	[kJ/kg]
m	Mass flow rate	[kg/s]
$\bar{m}$	Molar flow rate	[kmole/s]
p	Pressure	[bar]
$\bar{R}$	Universal gas constant, 8.314	[kJ/kmole,K]
s	Entropy	[kJ/kg,K]
$\bar{s}$	Entropy	[kJ/kmole,K]
t	Temperature	[°C]
T	Temperature	[K]
x	Mass fraction	
$\bar{x}$	Molar fraction	

Subscript

ch	chemical
g	gas
st	stream
f	fuel
ref	reference state

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