Thermodynamics analysis for high temperature hydrogen production system

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Abstract:

Using clean energy sources is considered as a prevention solution for global warming. Hydrogen is one of the most popular clean and renewable fuel which is widely noticed by researchers in different approaches from additive fuel of internal combustion engines to pure feed of fuel cells. Hydrogen production is also one of the most interested field of studies and extended efforts are doing to fined high performance, fast and economical ways of its production. In this work, a novel high temperature steam electrolyser system with main solar integrated Brayton cycle core is proposed and numerically simulated to achieve this goal. Energy and exergy analysis having better perception of system performance is done and Rankine and organic Rankine cycles were utilized cooperating with the main core to improve its efficiency. The influences of different parameters such as turbine inlet temperature, inlet heat flux from the sun, compression ratio and also used organic fluid were investigated based first and second laws. Results show the high performance of proposed system, more than 98% energy efficiency of hydrogen production, besides the simplicity of utilizing it. The most exergy destruction occurs in sun heat flux absorption of

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power generation system, more than 54%, and its performance can be increased improving heat absorbing technology.

**Keywords:** Energy-Exergy Analysis; HTSE; Renewable Energy; Solar Driven Cycle; ORC.

1. **Introduction:**

The world dependence on fossil fuels due to needs in transportation, buildings and electricity generation was sharply increased since the industrial revolution. Indeed, the life standards are increased as well as energy consumption. However, some concern such as climate change, global warming, acid rains, pollution, sea levels increasing and ozone layer depletion have been made utilizing fossil fuel in different approaches [1] and another energies have become much more vital [2]. Hydrogen has been presently considered by researchers as an alternative renewable and clean energy resource in different approaches, from methanol production [3] to pure/additive fuel in internal combustion engines [4-7]. Although hydrogen abundantly exists in the earth, it is just found in composition of other materials. In consequent, hydrogen production is now one of the most interested field of studies and extended works were done to improve its efficiency economically [8-10]. However, more studies are still needed to achieve more acceptable exergy efficiencies considering reported values by researchers and thermodynamics analysis of different systems is considered as a suitable way to improve under studying systems [11-13].

Using renewable sources to produce hydrogen, as sustainable hydrogen economy, can be categorized as two main groups; low and high temperature electrolyzing. High-temperature electrolyserers are more advantageous than low-temperature one because of good ion conduction at an elevated temperature [14, 15] while they need more inlet power and heat. Demanded heat and power can be provided by different thermodynamic cycles employing solar [16], wind turbine [17], nuclear [18] and geothermal [19] energy technologies. The solar based proposed system by Ozcan and Dincer [20] had overall 18.8% energy and 19.9% exergy efficiencies, respectively and they assert that these efficiencies can be improved to 26.9%
and 40.7% employing heat absorbed by the molten. Balta et al. [21] dividing their solar based system into the power generation and hydrogen production sections, reported that the energy and exergy performances of power generation system (PGS) are found 24.79% and 22.36%, respectively and for hydrogen production system are 87% and 88%. Indeed, a conceptual design of photovoltaic solar energy conversion was done by Bhattacharyya et al. [22] and proposed module thermodynamic and conversion efficiencies were estimated. Sayyaadi [23] utilized new set up for dual hydrogen-power generation plant. The nuclear based high temperature steam electrolysis (HTSE) proposed by Ozcan and Dincer [24] had also 18.6% and 31.35% energy and exergy efficiencies and the overall energy and exergy efficiencies of coal gasification based hydrogen production system proposed by Seyitoglu et al. [25] were 41% and 36.5% respectively. Also exergetic efficiency of biogas-based High temperature steam electrolysis hydrogen production proposed by Abuşoğlu et al. [26] was reported by 25.83%.

In this paper, a high temperature electrolyser is employed for hydrogen production and a Brayton cycle integrated by solar energy is used to provide electrolyser demanded heat and power. A Rankine and organic Rankine cycles (ORC) are also utilized for system performance efficiency enhancement and in addition to compare two working fluids of ORC, first and second law analysis of proposed system are done to find the best operation condition.

2. System Definition:

The proposed hydrogen production system has two main parts, namely hydrogen production and power generation. Hydrogen production section is adapted from ref. [27] that hydrogen is produced via HTSE method where the high temperature steam is divided into the pure hydrogen and oxygen by received electricity from PGS. Demanded heat is also provided from waste heat of PGS. Indeed, two heat exchangers are also utilized to use the heat of separated hot hydrogen and oxygen shown in Fig.1. More detail of HTSE and employed heat exchangers are available in [27].
Power generation section consists of three cycles, namely, Brayton, Rankine and ORC. The main demanded power and heat for electrolyser is produced by Brayton cycle. In this cycle, air is compressed in two stage compressor via inter-cooler which makes air temperature equal to the ambient one. Electrolyser feed water is pre-heated by inter-cooler waste heat absorption. Then compressed air is pre-heated in solar receiver and more heat is added to achieve the highest feasible temperature due to the erosion of the turbine blades, in combustion chamber. The energy of air is first converted to the power via turbine and second absorbed by pre-heated electrolyser feed water. In the following, extra energy of air is employed to run Rankine and ORC boilers respectively. Finally, a simple Rankine cycle and an ORC with regenerator are utilized to convert air extra energy to the power. The general characteristics of integrated system are reported in Table 1.

3. Model Description:

Applying first and second laws equations on each used component is needed to analyze the integrated system performance. Required equations are illustrated in this section and following assumptions are used simplifying the modelling:

- All sections (PGS and electrolyser) are modeled by Steady State Steady Flow (SSSF) process.
- The thermodynamic tables are used adopting needed data of air, water and \( CO_2 \) properties.
- Pure methane is used as fuel of combustion chamber.
- The outflows of the condensers of ORC and Rankine cycle are assumed saturated liquid.
- Air and combustion products are assumed as ideal gases.

Energy Analysis

Considering expressed assumptions, mass conservation and energy equation of each multi-inputs-multi-outputs component in SSSF process [28] can be written as,
\[\sum \dot{m}_e = \sum \dot{m}_i \]  
\[\dot{Q} - \dot{W} = \sum \dot{m}_e h_e - \sum \dot{m}_i h_i \]  

Here, \(\dot{m}\) and \(h\) are the mass flow rate and enthalpy and subscripts \(i\) and \(e\) refer to inlet and exhaust flows.

Ideal gases correlations employed for Brayton cycle [28],

\[Pv = R_u T \]  
\[h = C_p T \]  
\[u = C_v T \]

Here, the pressure, specific volume, temperature and internal energy of the working fluid are shown by \(P, v, T\) and \(u\) respectively. \(C_p\) and \(C_v\) refer to the special heats on constant pressure and volume, and \(R_u\) expresses the universal constant of gases. Considering ideal gas as working fluid of Brayton cycle, the out temperatures of compressors and turbine exhaust flows can be written as [28],

\[\frac{T_e}{T_i} = 1 - \eta_{\text{tur}} \left(1 - \left(\frac{P_e}{P_i}\right)^{\frac{k-1}{k}}\right) \]  
\[\frac{T_e}{T_i} = 1 - \eta_{\text{comp}} \left(1 - \left(\frac{P_e}{P_i}\right)^{\frac{k-1}{k}}\right) \]

In these equations, \(k\) is the special heat coefficients ratio and \(\eta_{\text{tur}}\) refers to the isentropic efficiency of turbine as well as \(\eta_{\text{comp}}\) for compressor. In case of steam turbines and pumps, the exhaust flows characteristics can be defined as [28],
\[ \eta_{\text{tur}} = \frac{h_i - h_e}{h_i - h_{es}} \]  
\[ \eta_{\text{pump}} = \frac{h_i - h_{es}}{h_i - h_e} \]  
\[ \eta_{\text{pump}} = \frac{h_i - h_{es}}{h_i - h_e} \]  

Here, index \( es \) refers to the isentropic operation. All heat exchangers processes are assumed isobar and sufficient working pressure of intercooler is calculated as [28],

\[ P_{\text{intercooler}} = \sqrt{P_1 P_4} \]  

The sum of generated/consumed powers by turbines, compressors and pumps called net power for each cycle and the net power to inlet heat ratio is called the thermal efficiency. As an example, for proposed Brayton cycle [28],

\[ \dot{W}_{\text{net}} = \dot{W}_{\text{GT}} + \dot{W}_{\text{comp1}} + \dot{W}_{\text{comp2}} \]  
\[ \dot{Q}_{\text{net}} = \dot{Q}_{\text{receiver}} + \dot{Q}_{\text{C,Ch}} \]  
\[ \eta_i = \frac{\dot{W}_{\text{net}}}{\dot{Q}_{\text{net}}} \]

The mass flow rates of inlet fuel, Rankine cycle, the feed water of hydrogen production section and ORC can be calculated considering the temperature gradient of the hot side of heat exchangers assuming adiabatic operations of them [28],

\[ \dot{m}_{\text{mix, C, p, mix}} (T_6 - T_5) = \dot{m}_{\text{fuel}} \eta_{\text{comb, LHV}} \]  
\[ \dot{m}_{\text{mix, C, p, mix}} (T_8 - T_7) = \dot{m}_{\text{water}} (h_{22} - h_{23}) \]  
\[ \dot{m}_{\text{mix, C, p, mix}} (T_9 - T_8) = \dot{m}_{\text{Rankine}} (h_{12} - h_{13}) \]
\[ \dot{m}_{\text{mix}} C_{\text{p,mix}} (T_{10} - T_y) = \dot{m}_{\text{ORC}} (h_{17} - h_{18}) \]  

(17)

Where, \( \eta_{\text{comb}} \) and LHV refer to the combustion process efficiency and low heating value of used fuel respectively which are considered as 0.98 and 47.13 \( \text{MJ/kg} \) [29]. In addition, \( \dot{m}_{\text{mix}} \) and \( C_{\text{p,mix}} \) are the mass flow rate and specific heat of the combustion products.

**Exergy analysis**

Second law analysis as another way of devices performance evaluating, can be done when the first law analysis of each component and the thermodynamic properties of each steam had been defined. So, exergy balance equation is introduced as [28],

\[ \dot{E}_x^Q + \sum \dot{m}_i e_x_i = \dot{E}_x^W + \sum \dot{m}_c e_x_c + I \]  

(18)

Where, \( \dot{E}_x^Q \), \( \dot{E}_x^W \), \( e_x \) and \( I \) are exergy transfer due to heat transfer, exergy transfer from work, specific exergy and destructed exergy, respectively. Total exergy for each steam is divided into the thermo-mechanical and chemical exergy as [28],

\[ e_x = e_{x_m} + e_{x_c} \]  

(19)

\[ e_{x_m} = (h - h_0) - T_0 (s - s_0) \]  

(20)

\[ e_{x_c} = \sum_{i=1}^{N} y_i e_{x_c}^{ch} + RT_0 \sum_{i=1}^{N} y_i \ln(y_i) \]  

(21)

Where, \( s \) and \( y_i \) are entropy and the mole fraction of fluid compositions and index 0 refers to the dead state which is define as working fluid properties in ambient pressure and temperature. Indeed, the exergy of fuel is defined by the semi-empirical equation from ref [30],
\[ \varepsilon = \frac{\text{ex}_{\text{fuel}}}{\text{LHV}} \]  

(22)

Where, \( \varepsilon \) is considered close to the unit. Exergy transfer by the work and passed heat from the system boundaries [28],

\[ \dot{E}x^w = \dot{W} \]  

(23)

\[ \dot{E}x^Q = \left( 1 - \frac{T_0}{T_s} \right) \dot{Q} \]  

(24)

Where, \( T_s \) refers to the temperature of heat source. Exergy efficiency as the more accurate criterion of system operation is introduced as the division of achieved exergy to consumed one [28],

\[ \psi = \frac{\dot{E}x_{\text{net}}}{\dot{E}x_i - \dot{E}x_e} \]  

(27)

For hydrogen production performance analysis, thermal efficiency is defined as the ratio of separated hydrogen LHV from feed water to heat entered to the system. For second law efficiency, the exergy of separated hydrogen is compared via inlet exergy,

\[ \eta_t = \frac{\dot{m}_{H_2, \text{sep}} LHV_{H_2}}{Q_{in}} \]  

(28)

\[ \psi = \frac{\dot{E}x_{H_2, \text{sep}}}{\dot{E}x_{in}} \]  

(29)

4. Results and Discussion:
As the proposed system is a novel idea, experimental data are not available to validate the results of model. So, each employed cycle is separately validated via given data from the previous study [21] which were shown in Table 2. The reliability of generated results from provided model is in the high level since the model has high accuracy in system performance prediction.

After thermodynamic characteristics definition of each steam, the home-made simulator model can calculate the performance of proposed system. The thermodynamic characteristics of each steam is reported in Table 3. The performance of overall system were evaluated using these data besides defined equations in model description section and the results were briefly reported in Table 4. While 7532 kW of total 8873 kW net power was produced by Brayton cycle, almost 90% of total irreversibility was also from this cycle. However, the first law efficiency of PGS and hydrogen production were achieved by 50.7% and 98.3% respectively.

Proposed system performance due to the change of Brayton turbine inlet temperature when the other inlet parameters were considered fixed are shown in Fig.2 and Fig.3. Demanded fuel was increased 36.8% to achieve 1600 K while the heat received from the sun had no change. Consumed fuel enhancement rate was greater than turbine out power one, so the ratio of power to added heat in combustion chamber were decreased slightly. Furthermore, the irreversibility of general system was increased due to the more temperature of heat transfer in heat exchangers and hydrogen production efficiency was decreased by 6% due to the fuel consumption increase caused by turbine inlet temperature enhancement. System response to input heat flux from the sun is shown in Fig.4 and considering fixed turbine inlet temperature, less fuel is needed when the input heat flux was increased. Consequently, the ratio of produced power and Hydrogen to consumed heat in combustion chamber were increased by 29% and 13%, respectively.

Produced power and efficiency of Brayton cycle are affected by compression ratio and to investigate the impact of it on system performance it was changed between 8 and 16. In Fig.5, first and second law efficiencies, produced power and irreversibility of Brayton cycle via compression ratio change were shown. All of them were increased by compression ratio enhancement cause of more turbine power
generation rate than compressor power consumption rate. Irreversibility was also increased by 4.5 kW due to the enhancement of mean working pressure of cycle. Considering Brayton cycle as the main power generation core of PGS, total power was increased as well as Brayton cycle. Indeed, more temperature gradient in the inter-cooler due to isentropic temperature enhancement in compressor, increased total irreversibility by 13.9% which is shown in Fig.6.

To investigate the role of working fluid on organic Rankine cycle performance, its energy and exergy parameters are compared employing two different working fluids namely, carbon dioxide (R744) and ammonia (R717) which are shown in Fig.7 and Fig.8. In case of using carbon dioxide as working fluid, less net power was achieved and irreversibility decreased 50% at ORC. The interaction of less power and irreversibility caused both more energy and exergy efficiencies when carbon dioxide employed as working fluid.

5. Conclusion:

In this work, a high temperature electrolyser integrated with a power generation system consist of a solar based Brayton cycle which is developed by Rankine and organic Rankine cycles for hydrogen production, was proposed and numerically simulated. Energy and exergy analysis are done and the main results are listed in the following,

- Proposed system have more than 98% efficiency in hydrogen production.
- Power generation section has around 50% first law efficiency.
- The most exergy destructor section is solar tower by losing more than 50% of inlet sun irradiance.
- Proposed Brayton cycle can be more sufficient focusing on irreversibility reduction of solar tower and combustion chamber.
- Turbine inlet temperature enhancement decrease both energy and exergy efficiencies.
- Organic Rankine cycle produce more power with less efficiency employing ammonia as working fluid.
Acknowledgment: Authors acknowledge the funding support of Babol Noshirvani University of Technology through Grant program No. BNUT/390051/98

References:


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Nomenclature

Abbreviation:

HTSE  High Temperature Steam Electrolysis
PGS   Power Generation System
ORC   Organic Rankine Cycle
LHV   Low Heating Value, \(kJ/kg\)
USUF  Uniform State Uniform Flow
SSSF  Steady State Steady Flow

English Symbols:

\(C_p\)  Specific heat at constant pressure, \(kJ/kgK\)
\(C_v\)  Specific heat at constant volume, \(kJ/kgK\)
\(Ex\)   Exergy, \(kJ\)
\(ex\)   Specific Exergy, \(kJ/kg\)
\(h\)    Specific Enthalpy, \(kJ/kg\)
\(l\)    Irreversibility, \(kW\)
\(k\)    Heat Transfer Coefficient Ratio
\(m\)    Mass, \(kg\)
\(P\)    Pressure, \(kPa\)
\(Q\)    Heat Transfer, \(kJ\)
\(R\)    Gas Universal Constant
\(s\)    Entropy, \(kJ/kgK\); Sun irradiance, \(W/m^2\)
\(T\)    Temperature, \(K\)
\(u\)    Specific Internal Energy, \(kJ/kg\)
\(v\)    Specific Volume, \(m^3/kg\)
\(V\)    Speed, \(m/s\), Volume \(m^3\)
\(W\)    Work, \(kJ\)

Greek Symbols:

\(\eta\)  First Law Efficiency
\(\rho\)  Density, \(kg/m^3\)
\(\psi\)  Second Law Efficiency

Subscript:

0     Dead State
1     Primary State
2     Final State
\(ch\) Chemical
\(comb\) Combustion
\(e\)   Exhaust
\(i, in\) Inlet
\(s\)   Source
\(sep\) Separated
\(tm\) Thermomechanical
Figure 1: The schematic of the proposed system
Figure 2: First law analysis of proposed system via turbine inlet temperature
Figure 3: Net power and irreversibility of PGS via turbine inlet temperature
Figure 4: First law analysis of proposed system via sun heat flux
Figure 5: First and second laws analysis of Brayton cycle via compression ratio
Figure 6: Net power and irreversibility of PGS via compression ratio of Brayton cycle
Figure 7: Net power ORC and PGS via ORC working fluid
Figure 8: Irreversibility, energy and exergy efficiencies of ORC via ORC working fluid
### Table 1: General characteristics of proposed system [21]

<table>
<thead>
<tr>
<th>Solar tower</th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Receiver height</td>
<td>65 m</td>
</tr>
<tr>
<td>Number of heliostats</td>
<td>69</td>
</tr>
<tr>
<td>Total area of heliostat field</td>
<td>8349 $m^2$</td>
</tr>
<tr>
<td><strong>Brayton Cycle</strong></td>
<td></td>
</tr>
<tr>
<td>Working fluid</td>
<td>Air</td>
</tr>
<tr>
<td>Turbine isentropic efficiency</td>
<td>0.92</td>
</tr>
<tr>
<td>Compressor isentropic efficiency</td>
<td>0.88</td>
</tr>
<tr>
<td>Compression ratio</td>
<td>11.2</td>
</tr>
<tr>
<td>Turbine power capacity</td>
<td>5670 kW</td>
</tr>
<tr>
<td><strong>Rankine Cycle</strong></td>
<td></td>
</tr>
<tr>
<td>Working fluid</td>
<td>Water</td>
</tr>
<tr>
<td>Turbine isentropic efficiency</td>
<td>0.91</td>
</tr>
<tr>
<td>Pump isentropic efficiency</td>
<td>0.88</td>
</tr>
<tr>
<td>Turbine inlet temperature</td>
<td>623.15 K</td>
</tr>
<tr>
<td>Turbine inlet pressure</td>
<td>3000 kPa</td>
</tr>
<tr>
<td>Turbine exit pressure</td>
<td>65 kPa</td>
</tr>
<tr>
<td>Turbine power capacity</td>
<td>1020 kW</td>
</tr>
<tr>
<td><strong>ORC</strong></td>
<td></td>
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<tr>
<td>Working fluid</td>
<td>CO2</td>
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<tr>
<td>Turbine isentropic efficiency</td>
<td>0.95</td>
</tr>
<tr>
<td>Pump isentropic efficiency</td>
<td>0.90</td>
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<tr>
<td>Turbine inlet temperature</td>
<td>453.15 K</td>
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<tr>
<td>Turbine inlet pressure</td>
<td>15000 kPa</td>
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<tr>
<td>Turbine exit pressure</td>
<td>7000 kPa</td>
</tr>
<tr>
<td>Turbine power capacity</td>
<td>445 kW</td>
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### Table 2: Comparison of reference and simulated data

<table>
<thead>
<tr>
<th>cycle</th>
<th>energy efficiency</th>
<th>exergy efficiency</th>
<th>exergy destruction $[kW]$</th>
<th>power generation $[kW]$</th>
<th>$\frac{m_{H_2,produced}}{m_{H_2,intered}}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rankine</td>
<td>38.7</td>
<td>38.79</td>
<td>47.71</td>
<td>50.7</td>
<td>206</td>
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<tr>
<td>ORC</td>
<td>25.28</td>
<td>25.34</td>
<td>40.55</td>
<td>32.52</td>
<td>376</td>
</tr>
<tr>
<td>Simple PGS (Overal)</td>
<td>24.79</td>
<td>24.79</td>
<td>22.36</td>
<td>27.15</td>
<td>17338</td>
</tr>
<tr>
<td>simple HTSE (Overal)</td>
<td>-</td>
<td>30.98</td>
<td>-</td>
<td>0.399</td>
<td>18130</td>
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Table 3: each steam characteristics of proposed system

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<tr>
<th>State NO</th>
<th>fluid</th>
<th>T [K]</th>
<th>P [kPa]</th>
<th>m [kg/s]</th>
<th>h [kJ/kg]</th>
<th>s [kJ/kgK]</th>
<th>ex [kJ/kg]</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Air</td>
<td>298.2</td>
<td>101.3</td>
<td>14.24</td>
<td>298.6</td>
<td>5.696</td>
<td>0.0</td>
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<tr>
<td>2</td>
<td>Air</td>
<td>434.9</td>
<td>339</td>
<td>14.24</td>
<td>436.7</td>
<td>5.73</td>
<td>127.9</td>
</tr>
<tr>
<td>3</td>
<td>Air</td>
<td>298.2</td>
<td>339</td>
<td>14.24</td>
<td>298.6</td>
<td>5.349</td>
<td>103.3</td>
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<tr>
<td>4</td>
<td>Air</td>
<td>434.9</td>
<td>1135</td>
<td>14.24</td>
<td>436.7</td>
<td>5.383</td>
<td>23102</td>
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<td>5</td>
<td>Air</td>
<td>903.6</td>
<td>1135</td>
<td>14.24</td>
<td>937.2</td>
<td>6.159</td>
<td>500.5</td>
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<tr>
<td>6</td>
<td>Air</td>
<td>1523</td>
<td>1135</td>
<td>14.24</td>
<td>1664</td>
<td>6.769</td>
<td>1045</td>
</tr>
<tr>
<td>7</td>
<td>Air</td>
<td>833.2</td>
<td>101.3</td>
<td>14.24</td>
<td>858.9</td>
<td>6.762</td>
<td>242.4</td>
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<td>Air</td>
<td>759.4</td>
<td>101.3</td>
<td>14.24</td>
<td>777.8</td>
<td>6.66</td>
<td>191.7</td>
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<td>Air</td>
<td>480.7</td>
<td>101.3</td>
<td>14.24</td>
<td>483.5</td>
<td>6.179</td>
<td>40.96</td>
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<td>391.9</td>
<td>101.3</td>
<td>14.24</td>
<td>393.1</td>
<td>5.971</td>
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<tr>
<td>11</td>
<td>H₂O</td>
<td>361.1</td>
<td>65</td>
<td>1.582</td>
<td>368.5</td>
<td>1.169</td>
<td>24.56</td>
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<tr>
<td>12</td>
<td>H₂O</td>
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Table 4: proposed system performance

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