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A REVIEW OF THE USE OF RANKINE CYCLE SYSTEMS FOR HYDROGEN PRODUCTION

PREGLED SISTEMOV Z RANKINOVIM PROCESOM ZA PROIZVODNJO VODIKA

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Abstract

The vast majority of steam power plants in the world are based on the Rankine cycle. It is a well-known, trustworthy process that uses water or water vapour as a working medium, which supplies heat from various primary energy sources: fossil fuels, renewable energy sources (solar energy, energy from wood biomass, etc.) or a combination of both. With the Rankine cycle, energy sources other than electricity can be produced, which can be used as the primary energy source for various applications. The present article focuses on the production of hydrogen in addition to electricity; therefore, two energy sources are obtained from the same system with a few modifications of the existing power plant for further exploitation. There are several processes for hydrogen production using the Rankine cycle; in the present article, two processes are focused on: using part of the electricity produced and obtaining hydrogen by electrolysis of water or using part of high quality steam (basically heat energy) in combination with electricity and obtaining hydrogen by a thermochemical copper-chlorine process. Each of these processes has its advantages and disadvantages, which are presented in the present article with an example model of a power plant.

Povzetek

Velika večina elektrarn na svetu, ki uporabljajo parni proces za proizvodnjo električne energije, temelji na Rankinovem procesu. Gre za dobro znan zanesljiv proces, ki kot delovni medij največkrat uporablja

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vodo oz. vodno paro, kateri lahko dovajamo toploto iz različnih primarnih virov energije – fosilna goriva, obnovljivi viri energije (sončna energija, energija iz lesne biomase ipd.) ali pa kombinacija obojih. S pomočjo Rankinovega procesa lahko proizvajamo tudi druge vire energije, razen električne energije, ki jih nato uporabimo kot primarni vir energije za različne aplikacije. Članek se fokusira na proizvodnjo vodika poleg električne energije, kar pomeni, da iz istega sistema pridobimo dva vira energije za nadaljnje izkoriščanje, s čimer z nekaj modifikacijami izkoristimo obstoječe elektroenergetsko postrojenje za več namenov. Obstaja več procesov za pridobivanje vodika s pomočjo Rankinovega procesa, toda v članku se bomo osredotočili na dva procesa, in sicer lahko uporabimo del proizvedene električne energije in vodik pridobivamo z elektrolizo vode, lahko pa uporabimo tudi del visokokakovostne pare (v bistvu toplotno energijo) v kombinaciji z električno energijo in vodik pridobivamo s termokemičnim baker-klorovim procesom. Vsak od omenjenih procesov ima svoje prednosti in slabosti, ki bodo predstavljene v članku na konkretnem primeru modela elektrarne.

1 INTRODUCTION

According to various forecasts, energy demand will strongly increase in the coming decades, so it makes sense to make the best of existing systems, especially through the optimization and production of clean energy sources. Hydrogen is certainly a clean source of energy (besides electricity) and highly applicable in several sectors, mainly in industry and transport.

Throughout the world, about 80% of electricity is generated from fossil fuels and nuclear energy, *[1]*. These power plants mostly use the Rankine cycle as a process to convert primary energy source to electricity and possibly heat. The aforementioned products of the Rankine cycle can be used to produce hydrogen by electrolysis (using solely by electricity) or by a thermochemical copper-chlorine (Cu-Cl) cycle (using heat and electricity). However, an even greater change for the better would be if the Rankine cycle used renewable energy sources as a primary energy source.

The present article deals with a model of a conventional steam power plant, in which part of the generated electricity and heat is used to produce hydrogen. The article contains an example of thermodynamic calculation and a comparison of two different cases.

2 RANKINE CYCLE AND HYDROGEN PRODUCTION

The process model is a Rankine cycle power plant, in which two different processes were taken into consideration. First, we remodelled a steam power plant to a cogeneration plant (adding process heater in the cycle), since the heat is required for the Cu-Cl cycle to produce hydrogen, *[2],* (see Fig. 1). For the second case, we made no changes in the Rankine cycle, since only electricity is required for the hydrogen production by electrolysis, *[3],* (see Fig. 2). In both cases, the operating conditions are steady, and the process operates throughout the year (8,760 hours).

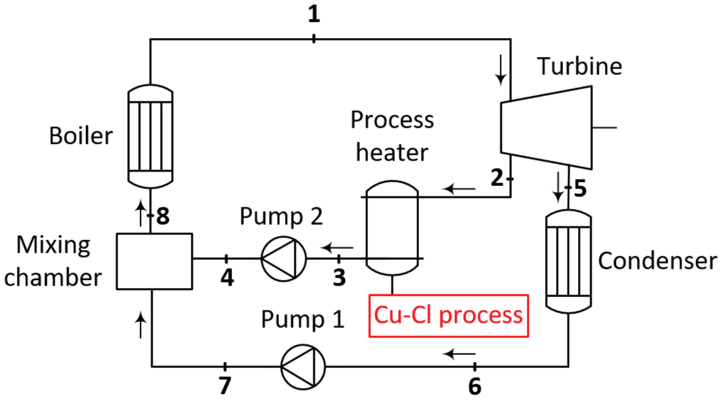

Figure 1: *Rankine cycle producing hydrogen by Cu-Cl process*

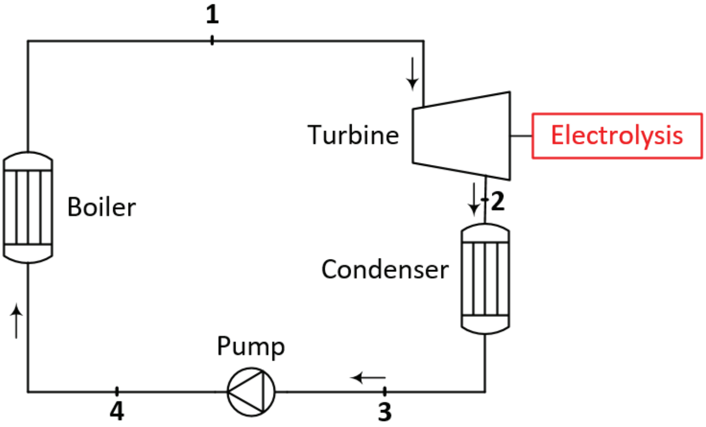

Figure 2: *Rankine cycle producing hydrogen by electrolysis*

Input data for the steam before entering the turbine are 8 MPa and 600 °C, and the mass flow rate is 50 kg/s. Pressure drops and heat losses are disregarded. Steam leaves the process heater and the condenser as a saturated liquid. The isentropic efficiency of the turbine is 80%; the pumps are isentropic.

In the first case, when producing hydrogen by the Cu-Cl process, 30% of the steam is extracted from the turbine at 5.5 MPa for process heating. As in *[2],* the maximum temperature required for the Cu-Cl cycle is 530 °C (see Fig. 3); therefore, the steam cannot expand to pressure lower than 5.5 MPa (temperature of the steam in state 2 (see Fig. 1) is 543 °C) before entering the process heater. Another 70% of the steam continues to expand to 5 kPa in the condenser.

In the second case, when producing hydrogen by electrolysis, the entire mass flow of the steam is expanded in the turbine from 80 MPa to 5 kPa in the condenser.

2.1 Thermochemical Cu-Cl cycle

In the copper-chlorine cycle, water is split into hydrogen and oxygen through intermediate Cu-Cl compounds. The maximum temperature in the cycle is 530 °C. The schematic of a Cu-Cl cycle is in Fig. 3, *[4]*. The chemical reactions of the four steps in the Cu-Cl cycle with the temperature range are, *[5]*:

$2CuCl_{(aq)} + 2HCl_{(aq)} \rightarrow H_{2(g)} + 2CuCl_{2(aq)}$ 90 °C

$CuCl_{2(aq)} \rightarrow CuCl_{2(s)}$ 150 °C

$2CuCl_{2(s)} + H_2O_{(g)} \rightarrow CuO \cdot CuCl_{2(s)} + 2HCl_{(g)}$ 400 °C

$CuO \cdot CuCl_{2(s)} \rightarrow 2CuCl_{(l)} + \frac{1}{2}O_{2(g)}$ 500 °C

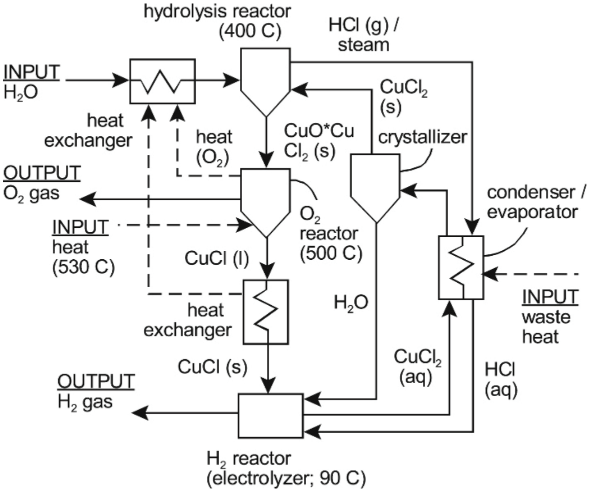

Figure 3: *Schematic of a Cu-Cl cycle*

The Cu-Cl cycle requires heat and electricity for hydrogen production. It has higher conversion efficiency than electrolysis and many other advantages over other methods for hydrogen production, including lower maximum temperature than other thermochemical cycles, *[2]*. Energy requirements for the process, used as input data for the calculation, are shown in Fig. 4, *[6]*.

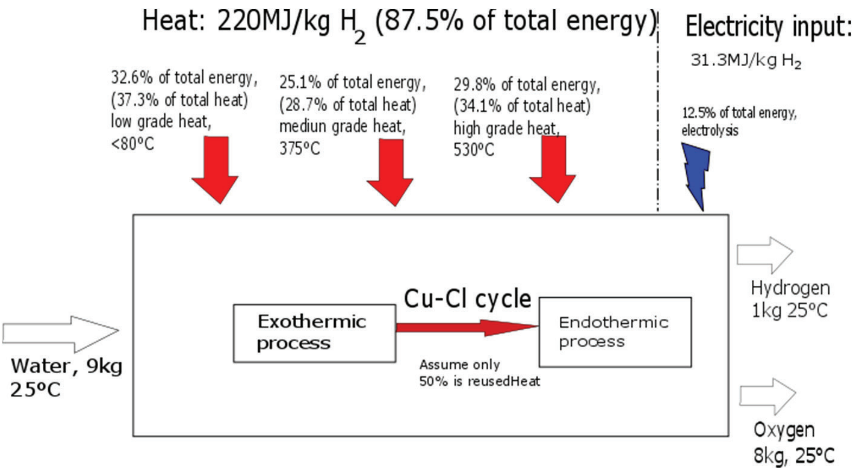

Figure 4: *Energy requirements for the Cu-Cl cycle*

We also took into consideration the amount of energy required to compress hydrogen; thus, the overall energy requirements for the production of 1 kg of hydrogen by Cu-Cl cycle are 220 MJ of heat and 31.3 MJ of electricity and for the compression 15 kWh of electricity, *[6]*.

2.2 Electrolysis

Electrolysis is a chemical process by means of which the reduction and oxidation of chemical compounds are made using a direct electric current to drive a chemical reaction. The electrolysis of water (also called water splitting) is a process by which water is decomposed into hydrogen and oxygen using a minimum electrical voltage of 1.229 V, *[3]*. The chemical reaction is:

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)}$$

In thermodynamic terms, the total enthalpy required to decompose water into hydrogen and oxygen is given by Eq. (2.1):

$$\Delta H = \Delta G + T\Delta S \tag{2.1}$$

In Eq. (2.1), ΔH is the reaction enthalpy, under standard conditions it is ΔH_f^0=-285.83 kJ/mol, ΔG is the difference in Gibbs free energy (required electricity) and TΔS is the amount of heat absorbed from the environment, *[3]*.

Also, in this case, we took into consideration the amount of energy required to compress hydrogen; thus, the overall energy requirements for the production of 1 kg of hydrogen by electrolysis are 55 kWh of electricity for hydrogen production and 15 kWh of electricity for its compression.

3 THERMODYNAMIC ANALYSIS

We made calculations for each of the cases mentioned above at the specified conditions. The process in Fig. 1 is also drawn in the T-s diagram and is shown in Fig. 5. In Table 1, all input data, pressures, and enthalpies at various steam states are collected for the case. When producing hydrogen by the Cu-Cl process, the rates of process heat supply and heat input, as well as the power produced, are given by Eq. (2.2), (2.3) and (2.4), *[7]*:

$$\dot{Q}_{PH} = 0.3\dot{m}_1(h_2\text{-}h_3) \tag{2.2}$$

$$\dot{Q}_{in} = \dot{m}_1(h_1\text{-}h_8) \tag{2.3}$$

$$\dot{W}_t = 0.3\dot{m}_1(h_1\text{-}h_2) + 0.7\dot{m}_1(h_2 - h_5) \tag{2.4}$$

Steam enters the turbine at state 1, 30% of steam is extracted from the turbine at state 2 for process heating; another 70% of steam expands further to state 5. Steam enters the condenser, where it is condensed at a constant pressure to state 6 and then pumped to state 7. After the process heater, the steam is saturated liquid (state 3) and then pumped to state 4. Both steam fractions enter the mixing chamber and leave it at state 8 (see Fig. 1 and 5).

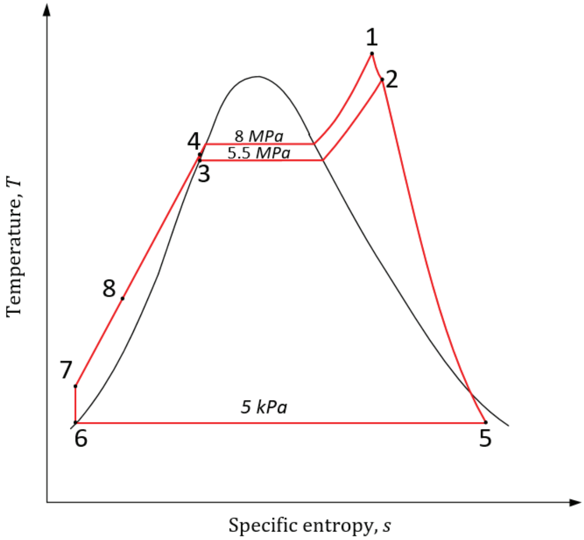

Figure 5: *T-s diagram Rankine cycle with process heater*

Table 1: *Input data, pressures and enthalpies for Rankine cycle with Cu-Cl process*

Steam state	Mass flow rate [kg/s]	Pressure [MPa]	Enthalpy [kJ/kg]
1	50	8	3642.38
2	15	5.5	3530.69
3	15	5.5	1185.09
4	15	8	1188.35
5	35	0.005	2427.33
6	35	0.005	137.75
7	35	8	145.79
8	50	8	458.56

In the second case, we have a basic Rankine cycle process without a process heater (see Fig. 2). The process is also drawn in the T-s diagram and is shown in Fig. 6. In Table 2, all input data, pressures, and enthalpies at various steam states are collected for that case. When producing hydrogen by electrolysis, the rate of heat input and the power produced are expressed in Eq. (2.5) and (2.6), *[7]*:

$$\dot{Q}_{in} = m(h_1\text{-}h_4) \quad (2.5)$$

$$\dot{W}_t = m(h_1\text{-}h_2) \quad (2.6)$$

Steam enters the turbine at state 1, and leaves it at state 2, then enters the condenser where it is condensed at a constant pressure to state 3 (saturated liquid) and pumped to state 4.

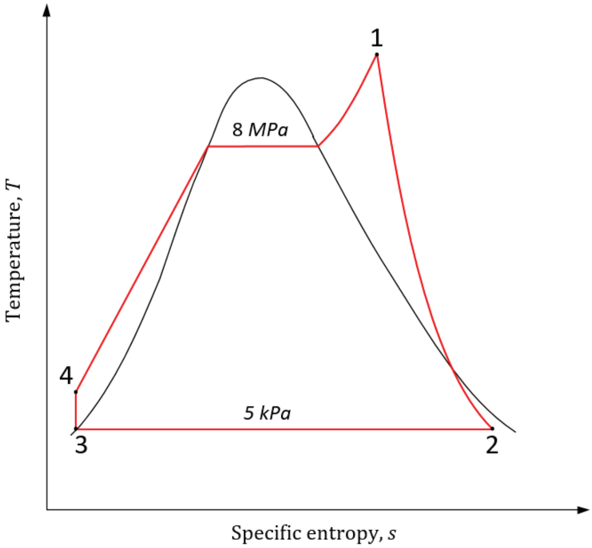

Figure 6: *T-s diagram Rankine cycle*

Table 2: *Input data, pressures and enthalpies for Rankine cycle with electrolysis*

Steam state	Mass flow rate [kg/s]	Pressure [MPa]	Enthalpy [kJ/kg]
1	50	8	3642.38
2	50	0.005	2441.24
3	50	0.005	137.75
4	50	8	145.79

For both cases, we calculated efficiencies. The Rankine cycle with a process heater is basically a cogeneration plant; the efficiency for this process is also called the "utilization factor", *[7],* and can be calculated by means of Eq. (2.7); the thermodynamic efficiency for the second case is written in Eq. (2.8). The power of the pumps is almost negligible, so this was not taken into consideration.

$$\epsilon_u = \frac{\dot{W}_t + \dot{Q}_{PH}}{\dot{Q}_{in}} \tag{2.7}$$

$$\eta_{TD} = \frac{\dot{W}_t}{\dot{Q}_{in}} \tag{2.8}$$

4 RESULTS AND DISCUSSION

When producing hydrogen by the Cu-Cl process, heat and electricity are required, so the Rankine cycle is used not only for electricity production but also for heat (process heating unit), resulting in lower turbine power output. With this cogeneration plant, the rate of process heat is 35.18 MW, and turbine power output is 44.2 MW. The rate of heat input in the boiler is 159.19 MW. Thus, the utilization factor, which was calculated with Eq. (2.7), is 50%.

The rate of process heat is the input data to calculate the amount of hydrogen produced by the Cu-Cl process. The system operates 8,760 hours per year, so the available heat is 308,177 MWh. This heat energy is enough to produce 5,043 tons of hydrogen per year or 13.82 tons of hydrogen per day. Then how much electricity is available per year and how much electricity is needed to produce 13.82 tons of hydrogen per day were calculated. Per year, 387,192 MWh of electricity is available; the amount of electricity required for the production and compression of 13.82 tons of hydrogen is 119,489 MWh, which means we use about 30.9% of generated electricity.

In a second case, producing hydrogen by electrolysis solely with electricity is required. With the basic Rankine cycle power plant, the turbine power output is 60.1 MW. The rate of heat input in the boiler is 174.83 MW. Thus the thermodynamic efficiency, which was calculated with Eq. (2.8), is 34.4%.

For an extreme case, which is impossible in practice, when all of the electricity generated in the Rankine cycle power plant is used for the hydrogen production and compression, the amount of produced hydrogen has been calculated. Per year 526,476 MWh of electricity is available, which is enough to produce 7,521 tons of hydrogen per year or 20.6 tons of hydrogen per day. If the same percentage of electricity as in the previous case (30.9% of generated electricity) is used, the amount of produced hydrogen would be 2,324 tons of hydrogen per year or 6.37 tons of hydrogen per day.

Thermodynamic results for both cases are shown in Table 3.

Table 3: *Calculation results*

	RC + Cu-Cl process	**RC + electrolysis**
$\dot{Q}_{PH}$ [MW]	35.18	/
$\dot{Q}_{in}$ [MW]	159.19	174.83
$\dot{W}_t$ [MW]	44.2	60.1
ϵ_u/η_{TD}	0.50	0.344
H_2 produced [t/day]	**13.82**	100 % of electricity **20.6**
		30.9 % of electricity **6.37**

The calculation results show that a higher amount of hydrogen is produced by the Rankine cycle with a process heater for the Cu-Cl process; since the use of 100% of generated electricity is not realistic, the power supply must always be provided, but there may be a surplus of generated electricity, which can be used for other purposes, such as hydrogen production. If only 30.9% of electricity generated is used, more than half as much hydrogen as in the first case can be produced. Perhaps it makes sense to use also heat, not only electricity but also for hydrogen production, since the electricity is more widely used for many other applications and is easily convertible into other forms of energy.

5 CONCLUSION

The present article shows that it makes more sense to produce hydrogen by Cu-Cl process when a Rankine cycle power plant is the source of heat and electricity to drive a hydrogen production process. The article also gives many cues for future work, such as increased efficiency with modifications of the Rankine cycle; adding reheating or regeneration. It would be interesting to make an exergy and economic analysis and then compare results. However, more accurate results would be obtained by building a dynamic model for the chosen hydrogen production process.

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Nomenclature

(Symbols)	(Symbol meaning)
h, H	enthalpy
G	Gibbs free energy
T	temperature
s, S	entropy
$\dot{Q}$	heat rate
$\dot{m}$	mass flow rate
$\dot{W}$	power
ϵ	utilization factor
η	efficiency