



Review

A review of the integration of the copper-chlorine cycle with other systems for hydrogen production

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ABSTRACT

There are different methods for hydrogen production, among which thermochemical cycles are particularly important. One of the most common thermochemical cycles is the copper-chlorine cycle. In this cycle, the water electrolysis process takes place during a thermo-chemical reaction, and copper chlorine is used as a thermochemical reaction intermediate. This cycle requires two factors to produce hydrogen: A heat source with a temperature of about 520 °C and electricity. For this reason, it is possible to use the hot waste gases of industries or parabolic through collector and heliostat field to provide its heat. To supply electricity for this cycle, various alternatives from the power grid and wind turbine to heat recovery in cycles that use low-temperature energy sources are considered. In this article, the integration of the copper-chlorine cycle with power generation systems has been discussed and investigated from the perspective of energy, exergy, and economics. This review is divided into two general parts using renewable and non-renewable resources. At the beginning of this article, various methods of hydrogen production focusing on the copper-chlorine cycle have been briefly discussed. In the following, the way this cycle works is explained along with energy, exergy, and economic equations, and the research done in this direction is explained. Finally, a strategy for how to integrate the copper-chlorine cycle with other systems is described. Studying this article, in addition to giving a better attitude in the field of integrating this cycle with other plants, is similar to a guideline for using the cycle along with other systems for better productivity. The conducted investigations showed that the recovery of hot industrial exhaust gas as a source of heat for the Cu-Cl cycle has a high potential for saving energy consumption and reducing environmental pollutants. To produce the required electricity, it is recommended to use cycles that work with a low-temperature energy source, such as the organic Rankine cycle and Kalina cycles. Also, if renewable energy sources are used, it is recommended to use parabolic through collectors and heliostats to produce the required heat. As in the case of non-renewable energy sources, cycles with low-temperature energy sources can be used.

1. Introduction

Various factors, such as limited fossil resources, negative environmental impacts, utilization of hydrocarbon resources, and rising prices of fossil fuels, are among the reasons that many energy and environment experts have encouraged to create of a new structure based on energy security,

environmental protection, and the improvement of system energy efficiency (ENE) [1, 2]. Accordingly, hydrogen is one of the best options to play the role of energy carrier in this new energy supply system [3]. Hydrogen gas can produce high energy by burning in the presence of oxygen and producing only water.

Symbols:			
A, B, C, ..., H	Constants of Shomate equations	n	Number of years
c	Specific cost (US\$/kW)	N	Annual duration of operation (hrs)
\dot{C}	Cost rate associated with a stream (US\$)	N	Project lifetime (equal to 25 years)
C_0	Total investment cost (US\$)	NPV	Net present value (US\$)
CRF	Capital recovery factor	P	Pressure (kPa)
Cu-Cl	Copper-Chlorine	PP	Payback period (years)
ex	Specific exergy (kJ/kg)	\dot{Q}	Heat transfer rate (kW)
\dot{E}	Exergy rate (kW)	r	Discount factor (%)
\dot{E}_x	Exergy rate (kW)	R	Universal gas constant, $R=8.314$ (kJ/kmol.K)
f_k	Exergoeconomic factor	s	Specific entropy (kJ/kg.K)
g	Gravitational acceleration (m/s ²)	SPP	Simple payback period (years)
h	Specific enthalpy (kJ/kg)	T	Temperature (K)
i	Inflation rate (%)	V	Velocity (m/s)
IRR	Internal rate of return	\dot{W}	Power (kW)
k	Specific cost of products (US\$/kWh)	x	Mass fraction
K	Investment and installation cost of component (US\$)	y	Mole fraction
LHV	Lower heating value (kJ/kg)	\dot{Z}	Capital investment (US\$)
m	Mass flow rate (kg/s)	Z	Height (m)
Abbreviations			
EDR	Exergy destruction rate	PSA	Pressure swing adsorption
EES	Equation engineering solver	PTC	Parabolic through collector
ENE	Energy efficiency	RO	Reverse osmosis
EXE	Exergy efficiency	SAM	System advisor model
HRSG	Heat recovery steam generator	SMOA	Static multi-objective optimization approach
HSR	Heliostat solar receiver	SRC	Steam Rankine cycle
MED	Multi effect distillation system	TEG	Thermoelectric generator
ORC	Organic Rankine cycle	TES	Thermal energy storage
PCM	Phase change material		
Greek Symbols			
η	Efficiency	φ	Maintenance factor
Subscripts			
0	Reference state condition (101.3 kPa, 25 °C)	i	Component number
ch	Chemical	in	Input
Cu-Cl	Copper-chlorine cycle	k	Component k
chi	Chemical exergy	out	Output
D	Destruction	w	Water
F	Fuel		

This energy can be used as fuel to move vehicles as well as spacecraft and rockets. Hydrogen as a renewable fuel can be considered an alternative to fossil fuels [4]. Today, hydrogen is mainly used in the production of methanol, ammonia, and oil refining. Hydrogen is also used in NASA's space program as fuel for spacecraft and in fuel cells that generate heat, electricity, and drinking water for astronauts [5]. Among the features that distinguish hydrogen from other fuels, alternatives are its abundance, almost very low emissions, reduction of greenhouse gases, and production cycle reversibility [6, 7]. Hydrogen production methods are divided into two general categories of use of renewable and non-renewable sources, which are as follows [8]: Hydrogen production from renewable sources:

- Photoelectrochemical [9]
- Biologically [10]
- Biochemical [11]
- Thermochemical [12, 13]
- Radiolysis of water [12, 13]
- Water electrolysis [14, 15]

Hydrogen production from non-renewable sources:

- Steam reformer [16]
- Auto-thermal [17]
- Pyrolysis [18]

Due to the need for lower temperatures than the thermal processes of hydrogen production, electrochemical cycles of hydrogen production have received special attention. These cycles typically produce hydrogen using heat sources and a series of chemical processes. The chemicals used in this cycle are reused to create a closed cycle. The input of this cycle is water, and its output is hydrogen and oxygen. The general types of these cycles have the following three steps [13, 19]:

- Hydrogen production
- Oxygen production
- Chemical material recovery

According to the research literature, there are more than 200 types of thermochemical cycles. But few types have become widespread and have been put to practical use. The most important types of these electrochemical cycles are as follows [20-23]:

- Copper-sulfate (Cu-SO₄)

- Copper–chlorine (Cu–Cl)
- Iron–chlorine (Fe–Cl)
- Cerium–chlorine (Ce–Cl)
- Vanadium–chlorine (V–Cl)
- Hybrid chlorine
- Magnesium–iodine (Mg–I)
- Cerium–chlorine (Ce–Cl)

Among the types of mentioned cycles, the Cu – Cl cycle has the following priorities [20, 24]:

- Low operating temperature
- Less setup and repair costs
- Consume less electricity
- Common chemical reactions require an adverse reaction

Given the importance of the Cu-Cl cycle and its superiority over other types of electrochemical cycles in the research literature, research is needed to examine this cycle in terms of energy, exergy, and economics. In this article, first, the processes performed in this cycle and its energy, exergy, and economic analyzes are presented. Also, the energy sources used to launch this cycle are examined, and their limitations and benefits are presented. Finally, a strategy for using this cycle to produce hydrogen is presented.

2. Process description

The Cu-Cl cycle is a four-step thermochemical cycle using copper chlorine intermediate to produce hydrogen. This cycle is a hybrid process that has both electrolysis and thermochemical steps. The maximum required temperature is about 530 °C. The thermochemical reactions performed, and the temperature range is shown in Table 1 [22].

Table 1. The Cu-Cl reactions performed the temperature range and the feed of each reaction

No.	Chemical steps	Temperature range (°C)
1	2CuCl(aq) + 2HCl (aq) +Thermal energy+electrical energy→ 2CuCl ₂ (aq)+ H ₂ (g)	<100
2	CuCl ₂ (aq)+ Thermal energy → CuCl ₂ (s)	<100
3	2CuCl ₂ (s) + H ₂ O (g)+ Thermal energy → + 2HCl (g)+CuO×CuCl ₂ (s)	400
4	CuO and CuCl ₂ (s)+ Thermal energy → 2CuCl (l) + 1/2O ₂ (g)	500

The Cu-Cl cycle has three different types that have several different steps. The number of steps of this cycle is 3, 4, and 5 steps. In the 5-step cycle, copper production is electrolytic. Then, it is transferred to a heat-generating hydrogen reactor and reacted to produce hydrogen with molten HCl and CuCl gas. The 4-step cycle combines these steps to eliminate the intermediate step of solid copper production and displacement from CuCl / HCl electrolysis. In the removed phase, electrolyte hydrogen and copper chlorine are produced. The aqueous product is then dried to produce copper chlorine particles. In a 3-step cycle, these steps are

produced by supplying aqueous copper chloride directly to the hydrolysis chamber of the same copper oxychloride product. The 3-step cycle requires the least electrical energy and the 5-step Cu-Cl cycle requires the least heat energy. If an efficiency of 40% is assumed to convert heat energy into electricity in power plants, the best option in terms of energy consumption is the 5-step Cu-Cl cycle [25].

3. Theoretical modeling

3.1 Mass and energy balance relations

In general, mass and energy balance relations can be written as follows [26]:

$$\sum_{in} \dot{m} = \sum_{out} \dot{m} \tag{1}$$

Where \dot{m} means mass flow rate.

$$\dot{Q} + \sum_{in} \dot{m} \left(h + \frac{v^2}{2} + gZ \right) = \sum_{out} \dot{m} \left(h + \frac{v^2}{2} + gZ \right) + \dot{W} \tag{2}$$

For the Cu-Cl cycle, the mass-energy balance equations can be written as follows:

$$\dot{m}_W + \dot{m}_{CuCl_2} = \dot{m}_{H_2} + \dot{m}_{O_2} + \dot{m}_{CuCl_2} \tag{3}$$

$$\dot{m}_W h_W + \dot{m}_{CuCl_2} h_{CuCl_2} + \dot{W}_{CuCl} + \dot{Q}_{CuCl} = \dot{m}_{H_2} h_{H_2} + \dot{m}_{O_2} h_{O_2} + \dot{m}_{CuCl_2} h_{CuCl_2} \tag{4}$$

Subscript W means water.

The molar base enthalpy in the Cu-Cl cycle is calculated according to the following equation [27, 28]:

$$\bar{h} - \bar{h}_0 = A T + B \frac{T^2}{2} + C \frac{T^3}{3} + D \frac{T^4}{4} - E \frac{1}{T} + F - H \tag{5}$$

In equation No .8, T is one-thousandth of the temperature (K). The values of the coefficients A to H are shown in references [27, 28].

The ENE for the Cu-Cl cycle is written as follows:

$$\eta_{energy\ Cu-Cl} = \frac{\dot{m}_{H_2} LHV_{H_2}}{\dot{W}_{CuCl} + \dot{Q}_{CuCl}} \tag{6}$$

The Cu-Cl overall efficiency is much higher than that of water electrolysis, which is powered by thermal power plants. Because in the Cu-Cl cycle, heat is directly used for hydrogen production. Whereas in a water electrolysis system, electricity must be generated by power generation systems, and the electricity generated is used for hydrogen production. Considering the efficiency of power plants, the efficiency of hydrogen production by water electrolysis device is about 30%, while in the Cu-Cl cycle, this value reaches 54%. If the heat loss of the systems is utilized for hydrogen production in the Cu-Cl cycle, the ENE will be higher [25].

3.2 Exergy balance relation

Exergy Maximum reversible useful work, from the initial state specified during a reversible process when it reaches environment equilibrium. Exergy is a compound property that depends on the conditions of the system in an additional environment. In the science of thermodynamics, exergy is divided into kinetic, potential, physical, and chemical types. Exergy per unit mass is called specific exergy, the equation of which is shown below [29, 30]:

$$ex = \sum x_i ex_{chi} + \frac{v^2}{2} + gZ + (h - h_0) - T_0(s - s_0) + T_0 \sum x_i R_i \ln y_i \tag{7}$$

The Cu-Cl materials standard chemical exergy in the dead state condition is presented in references [28, 31].

The molar base entropy in the Cu-Cl cycle is calculated as follows [27, 28]:

$$\bar{s} = A \times \ln(T) + B \times T + C \times \frac{T^2}{2} + D \times \frac{T^3}{3} - E \times \frac{1}{2T^2} + G \quad (8)$$

The exergy efficiency (EXE) for the Cu-Cl cycle is written as follows:

$$\eta_{\text{exergy Cu-Cl}} = \frac{\dot{m}_{H_2} \text{ex}_{H_2}}{W_{CuCl} + \dot{Q}_{CuCl} \left(1 - \frac{T_0}{T_{CuCl}}\right) + \dot{m}_{H_2O} \text{ex}_{H_2O}} \quad (9)$$

The exergy destruction rate (EDR) of the Cu-Cl cycle can be evaluated as follows:

$$\dot{E}_D = W_{CuCl} + \dot{Q}_{CuCl} \left(1 - \frac{T_0}{T_{CuCl}}\right) + \dot{m}_{H_2O} \text{ex}_{H_2O} - \dot{m}_{H_2} \text{ex}_{H_2} - \dot{m}_{O_2} \text{ex}_{O_2} \quad (10)$$

3.3 Economic evaluation

The payback period is one of the standard methods of evaluating economic plans, which is used by most financial analysts because it is easy to calculate. In this method, the criterion for evaluating the length time of investment return. Shorter payback plans are more attractive than longer payback plans. This method is especially useful when comparing two or more designs with each other. In reality, the payback period it takes for the net cumulative cash flows of the project to be zero. In other words, it takes time for the initial investment in the project to equal its returns. Simply put, it is the length of time that project costs are returned to investors. The payback period (PP) can be calculated by [32, 33]:

$$PP = \frac{\ln\left(\frac{CF}{CF-r.C_n}\right)}{\ln(1+r)} \quad (11)$$

Internal rate of return (IRR) means how much the company earns annually and on average by doing a project or an investment. The higher this coefficient, the more valuable the investment will be. This coefficient can be calculated by [32-34]:

$$IRR = \frac{CF}{C_n} \left[1 - \frac{1}{(1+IRR)^N}\right] \quad (12)$$

Net present value (NPV) in an investment is the difference between the cost to start investing and the present value of all the income streams from which the investment is made. The NPV answers the question of whether it is possible to make a relatively large return on investment. NPV can be calculated by the following relation [32-34]:

$$NPV = CF \frac{(1+r)^N - 1}{r(1+r)^N} - C_n \quad (13)$$

3.4 Exergoeconomic analysis

Exergoeconomic analysis is a combination of exergy and economic analysis to obtain more information about the exergy flow and product cost rates, and their relationship to investment costs. In this way, we can better understand the behavior of the system. The general equation of this analysis is as follows [35, 36]:

$$\sum_{in=1}^m \dot{C}_{in,l} + \dot{C}_{Q,l} + \dot{Z}_l = \sum_{out=1}^m \dot{C}_{out,l} + \dot{C}_{W,l} \quad (14)$$

The stream l cost rate is written as follows [35, 37]:

$$\dot{C}_l = c_l \dot{E}x_l \quad (15)$$

$\dot{E}x_l$ and c_l represent exergy and specified cost. The capital investment rate can be written as [35, 37]:

$$\dot{Z}_l = \frac{\phi Z_l \text{CRF}}{3600N} \quad (16)$$

In equation 16, CRF can be calculated by [35, 37]:

$$\text{CRF} = \frac{j(1+j)^m}{j(1+j)^m - 1} \quad (17)$$

j and m denote the interest rate and project lifetime. The exergy destruction cost is calculated by [35, 37]:

$$\dot{C}_{D,l} = c_{F,l} \dot{E}x_{D,l} \quad (18)$$

The exergoeconomic factor for component l can be calculated by [35, 37]:

$$f_l = \frac{\dot{Z}_l}{\dot{C}_{D,l} + \dot{Z}_l} \quad (19)$$

Therefore, the more the exergy component is degraded, the lower the economic exergy coefficient. For component l, high and low values of f_l indicate high investment and inefficient system performance, respectively.

4. The previous research

4.1 Renewable energy resource

Siddiqui et al. [38] have studied a triple production system with a new arrangement whose energy sources are solar and geothermal. Its subsystems include a flash steam geothermal power plant, an absorption chiller, a 4-step Cu-Cl electrochemical cycle, and a heliostat solar receiver (HSR). HSR provides the heat required for the Cu-Cl electrochemical cycle. The Cu-Cl electrochemical cycle waste energy is also used as the heat source of the absorption chiller generator. The products of this system are electricity (3398 kW), cooling (603.9 kW), and hydrogen (32.1 mole/s). Figure 1 depicts the layout of this system under study. The operating fluids for the geothermal power plant, HSR, and absorption chiller are water, molten salt, and water/ammonia solution, respectively. In this research, Aspen Plus software has been used to model the Cu-Cl electrochemical cycle, and Engineering Equation Solver (EES) software has been used for other components. The equations for ENE and EXE for this cycle are shown below [38]:

$$\eta_{\text{energy}} = \frac{W_{el,G} + \dot{Q}_{ABS} + \dot{m}_{H_2} \text{LHV}_{H_2}}{\dot{Q}_{\text{geothermal}} + \dot{Q}_{\text{solar}}} \quad (20)$$

$$\eta_{\text{exergy}} = \frac{W_{el,G} + \dot{Q}_{ABS,EV} \left(\frac{T_0}{T_{EV}} - 1\right) + \dot{m}_{H_2} \text{ex}_{H_2}}{\dot{E}_{\text{geothermal}} + \dot{Q}_{\text{solar}} \left(1 - \frac{T_0}{T_{\text{sun}}}\right)} \quad (21)$$

Subscripts ABS, and el, G denotes the cooling and net electrical production by the system. The sun's temperature is considered 5777 K. In the above energy equation, the output of the system, which includes the rate of hydrogen energy produced, cooling, and electricity, is divided by the sum of the system inputs, which include the rate of geothermal energy and solar radiation. While in the exergy equation, these values are calculated in terms of exergy flow. The ENE and EXE of this system are 19.6% and 19.1%, respectively, while the ENE and EXE of the Cu-Cl cycle are 35.3% and 35.9%, respectively. The COP and the EXE of the absorption chiller are 0.54 and 0.32, respectively. The highest rate of EDR is in steam turbines and the lowest in condensers. The efficiency of the above system depends to a large extent on the amount of solar radiation. For example, with increasing direct solar radiation

from 100 to 2300 (W/m²), ENE and EXE increase from 15.2% and 14.9% to 21.7% and 21.2%, respectively. The reason for this increase is the increase in the hydrogen production rate in the Cu-Cl cycle. According to previous studies, the ENE range of the flash steam geothermal power plant is between 10% and 17% [39], while the studied cycle [38] with the hybrid energy sources of solar and geothermal reached an energy efficiency of 19.6%, which is 2.6% higher than the highest efficiency range of the flash steam cycle geothermal power plant. Also, product diversity is another strength of this cycle. One of the problems of the system proposed in the ref [38] is the system control, how can two sources of solar energy that are not always available be controlled with a geothermal source to gain a stable production rate. Sadeghi et al. [40] studied a multi-generation system to produce electricity, steam, and hydrogen. The subsystems of this multigeneration system are SRC, gas turbine, HSR, thermal energy storage (TES) with phase change material (PCM), Cu-Cl cycle, and heat recovery. They used energy, exergy, and exergy-economic analyses to evaluate the system, as well as, system optimization via a non-dominated sorting genetic algorithm-II (NSGA-II) algorithm. The layout of the proposed multigeneration system is depicted in Figure 2. The proposed system of Ref [40] generates 370.8 kg/h hydrogen, 50.5 MW of electrical power, and 50.15 Ton/h steam. The Cu-Cl cycle consumes 5.18 MW of electrical power for 0.103 kg of hydrogen production. Also, the Cu-Cl purchase cost rate cycle accounts for 4.5% of the total system cost rate.

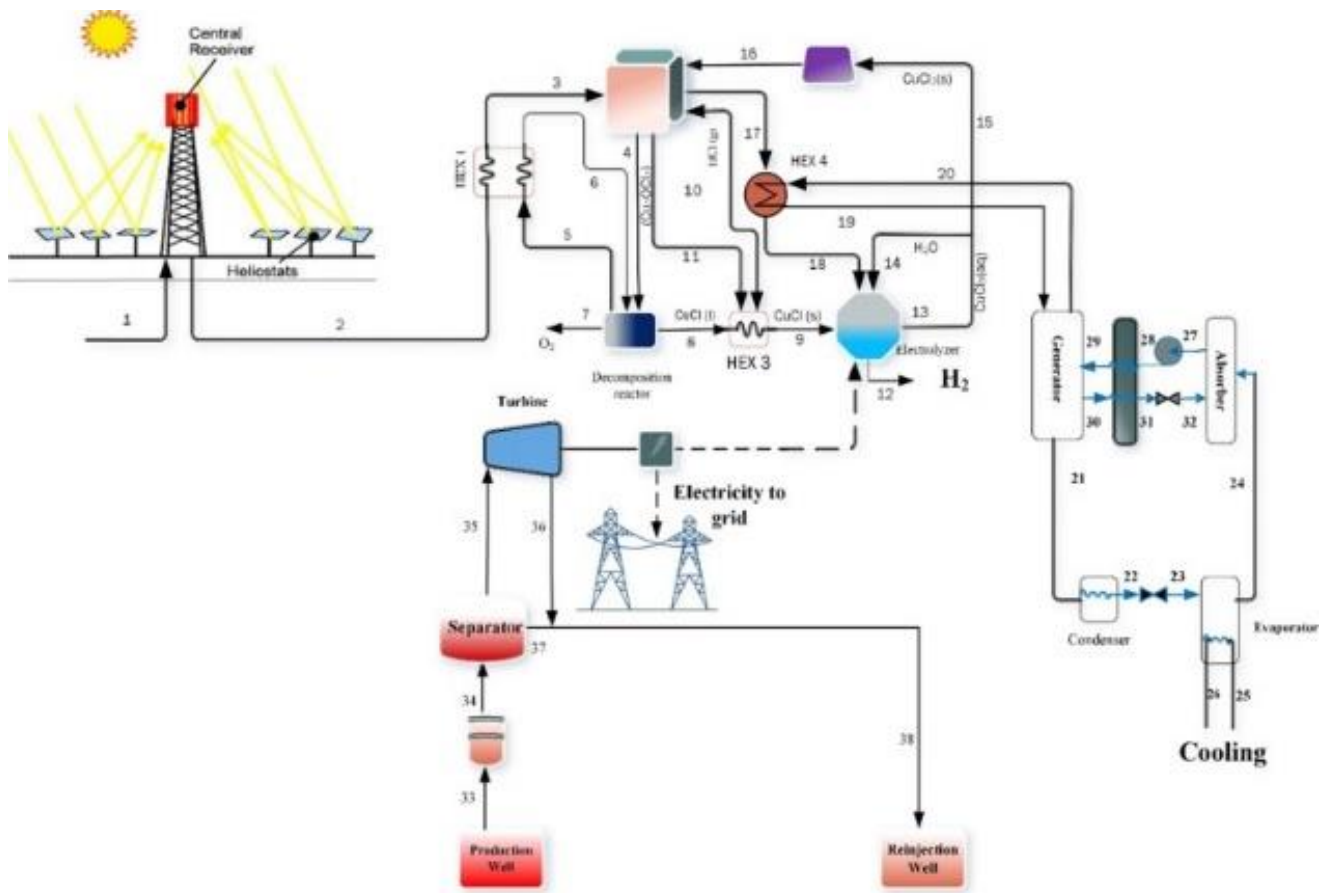
The system ENE and EXE can be calculated as follows [40]:

$$\eta_{\text{energy}} = \frac{W_{\text{net}} + \dot{Q}_{\text{Steam}} + \dot{m}_{\text{H}_2} \text{LHV}_{\text{H}_2}}{\dot{Q}_{\text{solar}}} \tag{22}$$

$$\eta_{\text{exergy}} = 1 - \frac{\dot{E}_d}{\dot{Q}_{\text{solar}} \left(1 - \frac{4}{3} \frac{T_0}{T_{\text{sun}}} + \frac{1}{3} \left(\frac{T_0}{T_{\text{sun}}} \right)^4 \right)} \tag{23}$$

In Ref [40], another method is used to calculate the system EXE. That is, instead of dividing the useful output exergy rate by the input exergy rate, the unit value is deducted from the ratio of the EDR to the input exergy rate. In both methods, the same value is calculated for the EXE of the system. The system ENE and EXE, and total EDR are 48.2%, 45%, and 111 MW, respectively. The Levelized cost of hydrogen and exergy are 10.9 US\$/GJ, and 1.6 US\$/kg, respectively.

Al-Zareer et al. [41] have evaluated a hydrogen production system utilizing solar energy. In this system, solar energy is converted to superheated steam by a one-megawatt HSR. Part of the steam in the five-step Cu-Cl cycle is used to generate hydrogen and remains in the SRC to generate electricity. The hydrogen produced is compressed up to about 700 Bar in a series of compressors. Cu-Cl and SRC components were modeled by Aspen Plus software. EES software was used for HSR simulation. This system produces 322 kW of electricity and 25.1 kg/h of hydrogen.



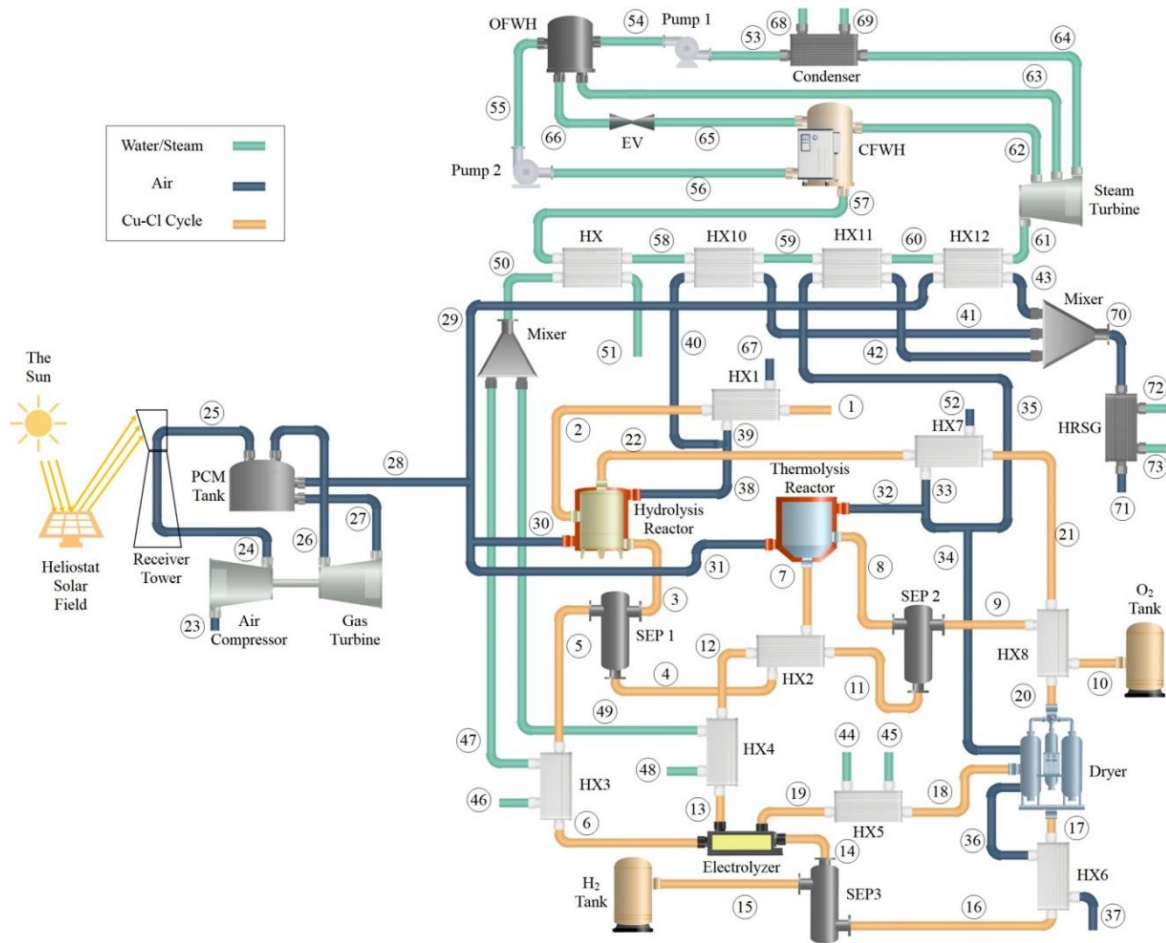


Figure 2. The layout of the system presented in Ref [40]

The ENE and EXE of this system can be calculated from the following equations [41]:

$$\eta_{energy} = \frac{W_{net} + \dot{m}_{H_2} LHV_{H_2} + \dot{m}_{H_2} h_{H_2}}{Q_{solar}} \quad (24)$$

$$\eta_{exergy} = \frac{W_{net} + \dot{m}_{H_2} ex_{H_2}}{Q_{solar} \left(1 - \frac{4}{3} \frac{T_0}{T_{sun}} + \frac{1}{3} \left(\frac{T_0}{T_{sun}} \right)^4 \right)} \quad (25)$$

By comparing equations 22 and 24, it can be seen that equation 24 has an extra term in the nominator of the system ENE equation. This is due to the compression of hydrogen up to a pressure of 700 bar by the proposed system related to this equation. The system ENE and EXE are reported to be 20.6% and 12.1%, respectively. The highest and lowest ENE is related to the HSR and hydrogen gas compression. In terms of EXE, the maximum and minimum values are related to the Cu-Cl cycle and hydrogen gas compression. The highest and lowest EDR is related to the HSR and the four-step Cu-Cl cycle, respectively.

From the mentioned results, it can be inferred that this integration is not suitable from the point of view of exergy. Because it does not improve the system ENE and EXE compared to the four-step Cu-Cl cycle. Dincer and Temiz [42] proposed a system including a parabolic concentrated solar power plant, steam Rankin cycle, fuel cell, and polymer electrolysis, two-face photovoltaic power plant, lithium bromide absorption chiller, and 4-step Cu-Cl cycle for electricity, cooling, and hydrogen generation.

Energy and exergy analyses have been performed for this system. The energy demand of this system is supplied by solar. Generally, for solar systems and due to their unavailability at night, storage systems are used, for which a molten salt storage system has been used. The function of this system is that the solar energy of parabolic through collector (PTC) and photovoltaic cells are converted into heat and electricity. The heat obtained is used in the Cu-Cl cycle to produce hydrogen and the rest is converted into electricity in steam turbines. The power consumption of the Cu-Cl cycle is supplied by the electricity generated by solar cells and steam turbines, and the rest goes to the consumer. Also, the heat dissipated by the steam turbine in the absorption chiller is converted into cooling. The proposed system configuration is shown in Figure 3. Similar to previous research, the Aspen Hysis is employed for Cu-Cl energy modeling. The ENE and EXE of this system are calculated from the following equations [42]:

$$\eta_{energy} = \frac{\dot{m}_{H_2} LHV_{H_2} + W_{net} + Q_{cooling}}{Q_{solar}} \quad (26)$$

$$\eta_{exergy} = \frac{\dot{m}_{H_2} ex_{H_2} + W_{net} + \dot{E}_{cooling}}{Q_{solar} \left(1 - \frac{4}{3} \frac{T_0}{T_{sun}} (1 - \cos \delta)^{\frac{1}{4}} + \frac{1}{3} \left(\frac{T_0}{T_{sun}} \right)^4 \right)} \quad (27)$$

In which, δ means deflection angle.

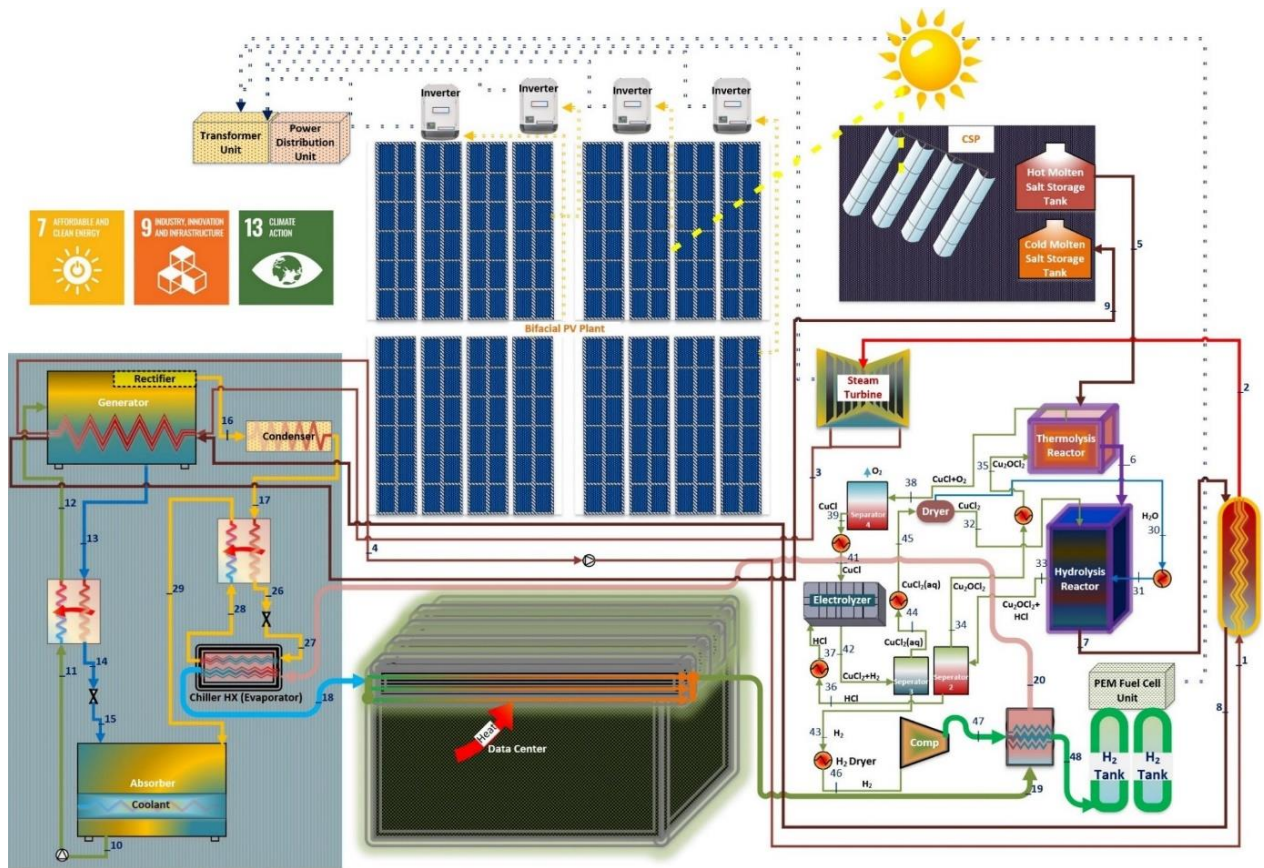


Figure 3. The proposed system configuration of Ref [42]

This system produces 315.9 kg/h of hydrogen, 22.7 MW of electricity, and 1.7 MW of cooling. The system ENE and EXE are reported at 36% and 31.2%, respectively.

Zhang et al. [43] have analyzed the energy, exergy, and economics of a solar system dual generating electricity and hydrogen. The optimization of this dual production system is done by the non-dominated sorting genetic algorithm II. The system's subsystems include a four-step Cu-Cl cycle, HSR, and molten salt heat storage, a Brayton cycle with an HRSG coupled by an organic Rankine cycle (ORC). To model this system, Aspen-Plus software, and Fortran programming language have been used. This cogeneration system produces 7.3 MW of electricity and 1.91 kg/h of hydrogen.

The system ENE and EXE are calculated by the following equations [43]:

$$\eta_{\text{energy}} = \frac{\dot{m}_{\text{H}_2} \text{LHV}_{\text{H}_2} + \dot{W}_{\text{net}}}{\dot{Q}_{\text{solar}}} \quad (28)$$

$$\eta_{\text{exergy}} = \frac{\dot{m}_{\text{H}_2} \text{ex}_{\text{H}_2} + \dot{W}_{\text{net}} + \dot{E}_{\text{cooling}}}{\dot{Q}_{\text{solar}} \left(1 - \frac{4}{3} \frac{T_0}{T_{\text{sun}}} + \frac{1}{3} \left(\frac{T_0}{T_{\text{sun}}} \right)^4 \right)} \quad (29)$$

The ENE and EXE, as well as the EDR of this dual system, is reported to be 28.9% and 46.2%, and 165.3 MW respectively. The price of hydrogen produced by this system is estimated at 2.84 US\$/kg. The payback period of this system with an initial investment of 60.85 million US\$ equals 2.5 years. Using the optimization algorithm, the system exergy efficiency increases to 50.9%, and the price of hydrogen produced decreases by 1.28 US\$/kg.

Quagued et al. [44] have studied the potential of using PTC with the solar tracking system to supply the required heat for the four-step Cu-Cl cycle in the climatic conditions of Algerian cities in Algeria. In this plan, the electricity needed for the cycle is provided by external sources. The working fluid in the PTC is Syltherm 800, which has stable conditions at high temperatures. In this article, information about the software used to analyze this system has not been given.

The ENE and EXE of this system are as follows:

$$\eta_{\text{energy}} = \frac{\dot{m}_{\text{H}_2} \text{LHV}_{\text{H}_2}}{\dot{Q}_{\text{solar}} + \dot{W}_{\text{in}}} \quad (30)$$

$$\eta_{\text{exergy}} = \frac{\dot{m}_{\text{H}_2} \text{ex}_{\text{H}_2}}{\dot{E}_{\text{solar}} + \dot{W}_{\text{in}}} \quad (31)$$

The hydrogen produced by this system is reported as 0.0125 kg/m²/h. The Cu-Cl ENE without considering the PTC is equal to 40.4% and the EXE of this system is equal to 92.2%. These values of ENE and EXE are within the range of references [45, 46]. Temiz and Dincer [47] have investigated the multiple production systems of electricity, heating, hydrogen, and freshwater, the energy required of which is supplied by geothermal and solar sources. The subsystems of this integrated system include a 4-step Cu-Cl electrochemical cycle, geothermal power plant, multi-effect distillation systems (MED), PTCs, molten salt storage system, solar heat pump, and three-step SRC whose operating fluid is ammonia. The products of this integrated system are fresh water, heating, electricity, and hydrogen.

The electricity production of this system is 1.65 kW with a price of 0.03 US\$/kWh. Also, the hydrogen production rate of the mentioned system is 0.01 kg/s with a price of 2.84 US\$/kg. The production rate of heat and potable water in this system is equal to 15.7 kW with a price of 0.005 US\$/kWh and the production rate of water is equal to 0.005 kg/s and its price is equal to 0.007 US\$/liter.

In this analysis, a hypothetical city near the Geyser region of California is considered. This city has the largest sources of geothermal energy. For energy, exergy, and economic simulation the system advisor model (SAM), Hysys, and EES software are employed.

The overall ENE and EXE of this integrated system are as follows [47]:

$$\eta_{\text{energy}} = \frac{\dot{m}_{\text{H}_2} \text{LHV}_{\text{H}_2} + W_{\text{net}} + \dot{m}_{\text{PW}} h_{\text{PW}} + \dot{Q}_{\text{heating}}}{\dot{Q}_{\text{solar}} + \dot{Q}_{\text{geothermal}}} \quad (32)$$

$$\eta_{\text{exergy}} = \frac{\dot{m}_{\text{H}_2} \text{ex}_{\text{H}_2} + W_{\text{net}} + \dot{E}_{\text{heating}} + \dot{m}_{\text{PW}} \text{ex}_{\text{PW}}}{\dot{E}_{\text{solar}} + \dot{E}_{\text{geothermal}}} \quad (33)$$

The ENE and EXE of this integrated system are equal to 27.4% and 13.7%, respectively.

In the continuation of this research, Sohani et al. [48] have optimized this system using NSGA-II and TOPSIS algorithms. Then, they compared the optimization results with the results of the static multi-objective optimization approach (SMOA) algorithm. This method was a comparison between static and dynamic optimization algorithms. Optimization variables include geothermal mass flow rate and hydrogen storage pressure. The objective functions are the amount of production of electricity, fresh water, hydrogen, heat, ENE, and EXE of the system and PP. By using the mentioned methods, the annual production of electricity, hydrogen, heat, and freshwater increased by 14.4, 13.5, 16.1, and 14.3%, respectively. Also, the annual efficiency of energy and exergy increased by 3 and 5.2%, respectively. Sadeghi and Ghandehariun [49] analyzed the energy and exergy of a triple-production solar system of electricity, steam, and hydrogen. They have also optimized the desired system with a genetic algorithm. This integrated system includes a solar power tower, a four-step Cu-Cl cycle, a eutectic fluoride salt PCM storage system, HRSG, and SRC. The solar energy tower is used to provide heat for the Cu-Cl cycle and the waste heat of this cycle is used to provide heat for the steam cycle. The layout of this system is presented in Figure 4.

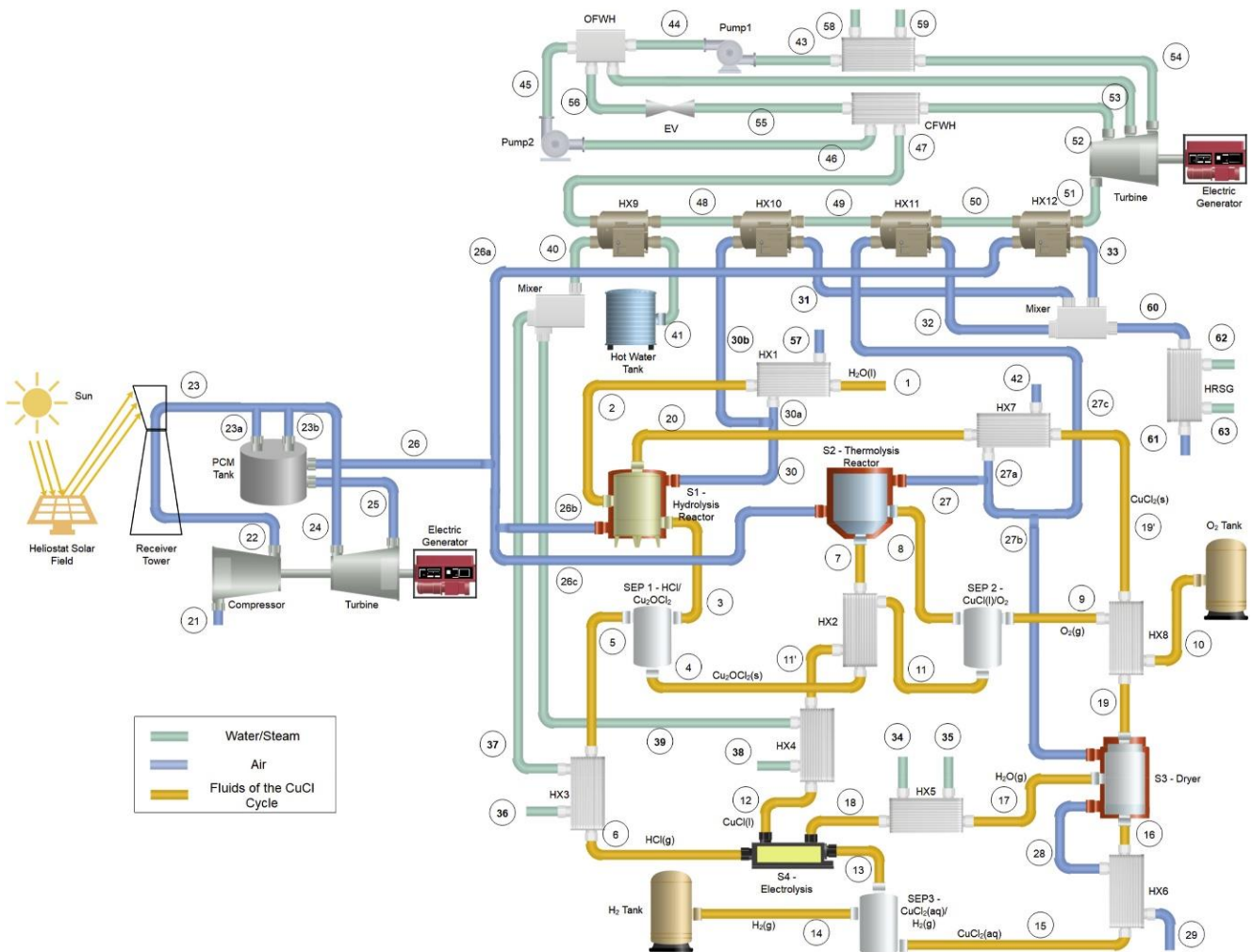


Figure 4. The layout of the system presented in reference [49]

The air is first compressed and it enters the solar receiver to be heated. The air is used to charge the PCM when there is enough solar radiation, and it is heated by the PCM when there is not enough solar radiation. Then the heated and compressed air is used to rotate the gas turbine and then it is returned to the PCM storage tank for a second time to be heated enough. After that, it is used as a heat source for the Cu-Cl cycle, heat exchangers, and SRC. In basic mode, this integrated triple-production system produces 41.7 MW of electricity, 343 kg/h of hydrogen, and 41 Ton/h of steam. The ENE and EXE of this system can be written as follows:

$$\eta_{\text{energy}} = \frac{\dot{m}_{\text{H}_2}\text{LHV}_{\text{H}_2} + W_{\text{net}} + \dot{Q}_{\text{steam}}}{\dot{Q}_{\text{solar}}} \quad (34)$$

$$\eta_{\text{exergy}} = \frac{\dot{m}_{\text{H}_2}\text{ex}_{\text{H}_2} + W_{\text{net}} + \dot{E}_{\text{steam}}}{\dot{E}_{\text{solar}}} \quad (35)$$

The ENE and EXE of this system are 45.1% and 49.0%, respectively. The highest share of the EDR is related to the solar system and the lowest amount is related to the Cu-Cl cycle and SRC. By optimizing this system, the amount of hydrogen produced increases by about 43%. Ishaq et al. [50] have studied the thermodynamic analysis of a triple production system of electricity, heat, and hydrogen, whose sources are solar and wind. The subsystems of this plant are a 4-step Cu-Cl electrochemical cycle, wind turbine, HSR, and hydrogen compression system. Three compressors are used in this system, whose pressure ratios are equal to 5, 10, and 15, respectively. The working fluid of the HSR is molten salt. The wind turbine's electrical production is equal to 17505 kW, of which 5605 kW is consumed by the compressors used to compress the hydrogen gas, and the power output of this system is equal to 11900 kW. The hydrogen production rate of this system is equal to 455.1 kg/h. The system ENE and EXE are as follows [50]:

$$\eta_{\text{energy}} = \frac{\dot{m}_{\text{H}_2}\text{LHV}_{\text{H}_2} + W_{\text{net}}}{\dot{Q}_{\text{solar}} + W_r} \quad (36)$$

$$\eta_{\text{exergy}} = \frac{\dot{m}_{\text{H}_2}\text{ex}_{\text{H}_2} + W_{\text{net}}}{\dot{E}_{\text{solar}} + W_r} \quad (37)$$

The subscript r shows the rated power of the wind turbine. The ENE and EXE of this dual production system are 48% and 49%, respectively.

4.2 Non-renewable energy resource

Ishaq et al. [51] have investigated the energy and exergy of a system that has produced electricity, hydrogen, and drinkable water using the wasted energy of the glass factory. The subsystems of this new arrangement include SRC, a four-step Cu-Cl cycle, ORC, MED, and a hydrogen compression system by series compressors. The arrangement of this cycle is shown in Figure 5.

The way this system works is that a part of the waste heat of the glass factory is utilized as a heat source for the 4-step Cu-Cl cycle and a part is used to produce steam in the SRC. Some of the waste heat of the SRC condenser is used as the heat source of the ORC cycle, whose operating fluid is Iso-butane. The remaining amount is used for the MED system to produce potable water. Using three series compressors, the hydrogen produced in this system is compressed to a 750 Bar pressure. EES and Aspen plus software have been used to simulate this system. If the hot gas exiting the glass factory has a temperature and flow rate equal to 1127 °C and 2500 kg/h,

the electricity produced by the SRC steam turbine and the first and second ORC turbines is 725, 727, and 697 kW, respectively. The ENE and EXE of this system are calculated from the following equations [51]:

$$\eta_{\text{energy}} = \frac{\dot{m}_{\text{H}_2}\text{LHV}_{\text{H}_2} + \dot{m}_{\text{PW}}h_{\text{PW}} + W_{\text{net}}}{\dot{Q}_{\text{in}}} \quad (38)$$

$$\eta_{\text{exergy}} = \frac{\dot{m}_{\text{H}_2}\text{ex}_{\text{H}_2} + \dot{m}_{\text{PW}}\text{ex}_{\text{PW}} + W_{\text{net}}}{\dot{E}_{\text{in}}} \quad (39)$$

The ENE and EXE of this integrated system are equal to 36.5% and 38.1%, respectively.

Ishaq and Dincer [52] have investigated the energy and exergy of a system with a new arrangement to recover the heat of the 805 °C hot gas from the exhaust of a factory (the type of factory is not specified). The mentioned system has HRSG, a thermoelectric generator (TEG), reverse osmosis (RO), pressure swing adsorption (PSA), ORC, an ammonia production reactor, and a four-step Cu-Cl cycle. The products of this system include electricity, hydrogen, fresh water, and ammonia that the above system produces 43.2 kg/h of hydrogen and 160.0 kg/h of ammonia.

The way this system works is that the hot gas from the factory turns the RO water into steam. This steam is converted into hydrogen in the Cu-Cl cycle. Hydrogen produced together with nitrogen produced by the PSA system is converted into ammonia in the ammonia production reactor. The heat of oxygen produced by the Cu-Cl cycle is recovered in the ORC and TEG subsystems to generate electricity. The produced electricity meets the electrical energy needs of other subsystems.

The ENE and EXE of this system are calculated from the following equations [52]:

$$\eta_{\text{energy}} = \frac{\dot{m}_{\text{H}_2}\text{LHV}_{\text{H}_2} + \dot{m}_{\text{NH}_3}\text{LHV}_{\text{NH}_3} + \dot{m}_{\text{FW}}h_{\text{FW}}}{\dot{Q}_{\text{in}} + W_{\text{net}}} \quad (40)$$

$$\eta_{\text{exergy}} = \frac{\dot{m}_{\text{H}_2}\text{ex}_{\text{H}_2} + \dot{m}_{\text{FW}}\text{ex}_{\text{FW}} + \dot{m}_{\text{NH}_3}\text{ex}_{\text{NH}_3}}{\dot{E}_{\text{in}} + W_{\text{net}}} \quad (41)$$

The system ENE and EXE are reported as 28.7% and 40.8%, respectively.

Fan et al. [12] have studied and analyzed the tri-generation system of electricity, cooling, and hydrogen by energy, exergy, and economic methods. This tri-generation system includes a gas turbine, a 4-step Cu-Cl electrochemical cycle, an absorption chiller, a heat recovery steam generator (HRSG), and an auxiliary boiler. The energy source of this system is natural gas a non-renewable energy source. The arrangement of this tri-generation system is shown in Figure 6.

The EES software is used to model this system. The tri-generation system produces 9.3 MW of electricity, 50.65 MW of cooling, and 84.9 kg/h of hydrogen.

In this system, 66.2 MW of electricity is generated by a gas turbine, which due to the power consumption in the Cu-Cl cycle of 56.2 MW and 0.7 MW by 50 absorption chiller units, the net electrical power is reduced to 9.3 MW.

The ENE and EXE equations of this triple production system are written as follows [12]:

$$\eta_{\text{energy}} = \frac{\dot{m}_{\text{H}_2}\text{LHV}_{\text{H}_2} + W_{\text{net}} + Q_{\text{cooling}}}{\dot{m}_{\text{NG}}\text{LHV}_{\text{NG}}} \quad (42)$$

$$\eta_{\text{exergy}} = \frac{\dot{m}_{\text{H}_2}\text{ex}_{\text{H}_2} + W_{\text{net}} + \dot{E}_{\text{cooling}}}{\dot{m}_{\text{NG}}\text{ex}_{\text{NG}}} \quad (43)$$

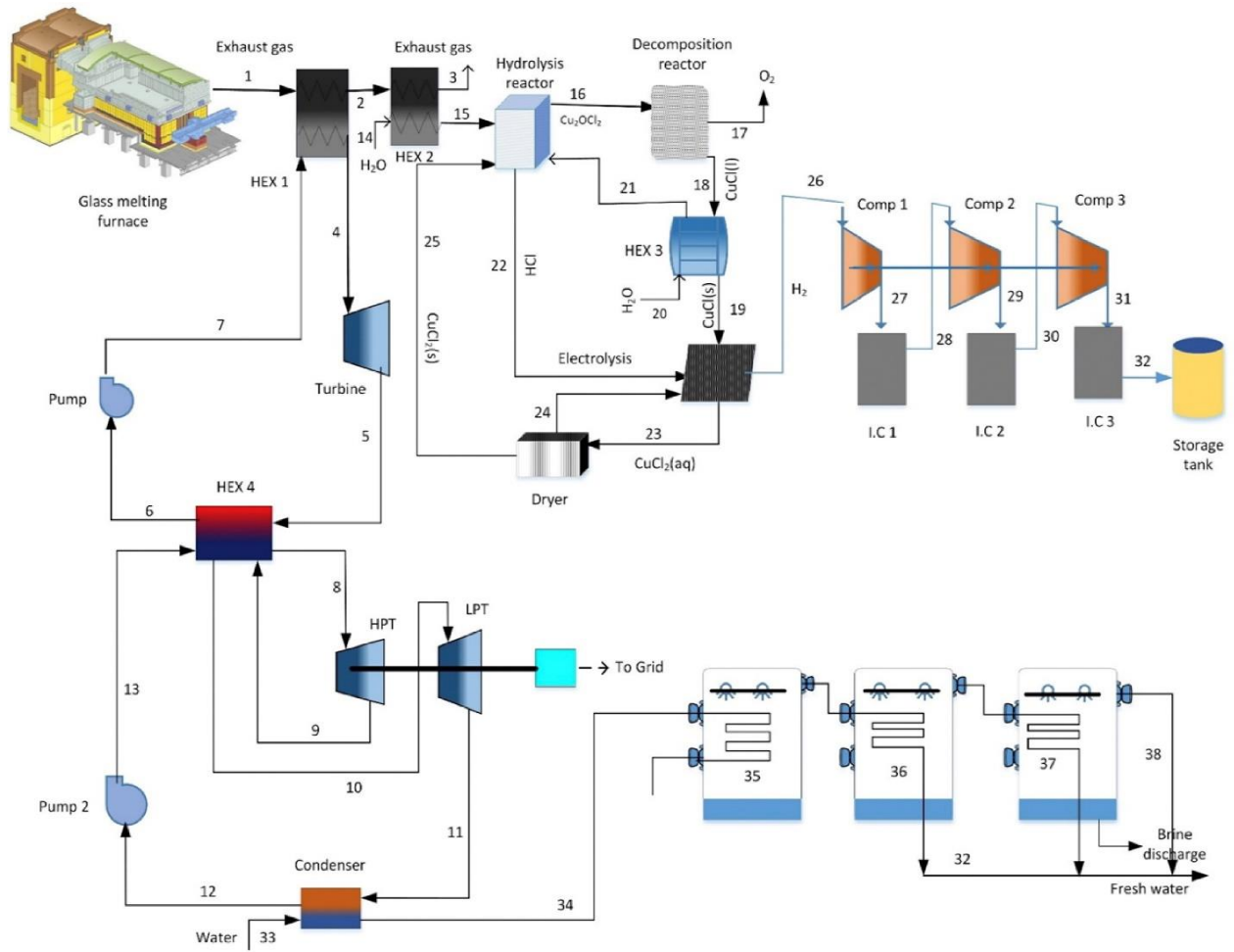


Figure 5. The arrangement of the cycle presented in Ref [51]

The heat of exhaust hot gas from the gas turbine for cooling and hydrogen production has a positive effect on system ENE so that by adding a 4-step Cu-Cl cycle, and an absorption chiller, system ENE increases from 19% to 29%, 43%, respectively. In the case of EXE, this increase is greater. EXE increases from 15% to 43.5%, and 44%, respectively. By comparing ENE and EXE, it can be concluded that adding an absorption chiller to the system has less effect on the system EXE compared to ENE. The highest rate of EDR is related to a gas turbine and 50 units of an absorption chiller and the lowest amount is related to the auxiliary boiler and Cu-Cl cycle. This tri-generation system arrangement has an economic justification. Incorporating the Cu-Cl cycle and subsequent absorption chillers reduces the payback time from 8.2 to 3.3 and 2.5 years, respectively.

Ishaq and Dincer [53] have done the energy and exergy analyses of a new system that uses the heat of cement furnace slag (temperature around 1200 to 1600 °C) in the Cu-Cl cycle. With this method, hydrogen is produced and finally, it is converted into ammonia in the system. In this research, two furnaces have been considered. In addition to the Cu-Cl cycle, the sub-systems used include an HRSG, SRC, ammonia generator reactor, and cryogenic air separator. They used Aspen Plus software for this evaluation. The electricity required in the Cu-Cl electrochemical cycle is provided by the

SRC. The final products of this system include electricity, ammonia, oxygen, hot water, and heat. The ENE and EXE of the system are calculated by the following relations [53]:

$$\eta_{energy} = \frac{\dot{m}_{NH_3} LHV_{NH_3} + W_{net} + \dot{m}_{O_2} h_{O_2} + \dot{Q}_{heating} + \dot{Q}_{HW}}{\dot{Q}_{in}} \quad (44)$$

$$\eta_{exergy} = \frac{\dot{m}_{NH_3} ex_{NH_3} + W_{net} + \dot{E}_{heating} + \dot{E}_{HW} + \dot{m}_{O_2} ex_{O_2}}{\dot{E}_{in}} \quad (45)$$

HW denotes hot water.

The electricity produced is equal to 3433 kW, and the hydrogen and ammonia produced are equal to 140.4 and 795 kg/h, respectively. The ENE and EXE of this system are equal to 36.1% and 30.1%, respectively.

Sayyadi [54] has investigated the integrated system of gas Brayton cycle with HRSG, and Cu-Cl thermochemical cycle via energy, exergy, and economic point of view. In this system, electricity is generated in the gas cycle and the hot exhaust gas is utilized to convert water into superheated steam. Superheated steam is used as the heat source of the Cu-Cl cycle. Also, a part of the electricity produced in the gas cycle is consumed in the Cu-Cl cycle. MATLAB software was used for the simulation of this proposed system. He examined 39 gas turbine models and finally found that the Mitsubishi HI 501 F model has the best performance for the arrangement of the proposed system.

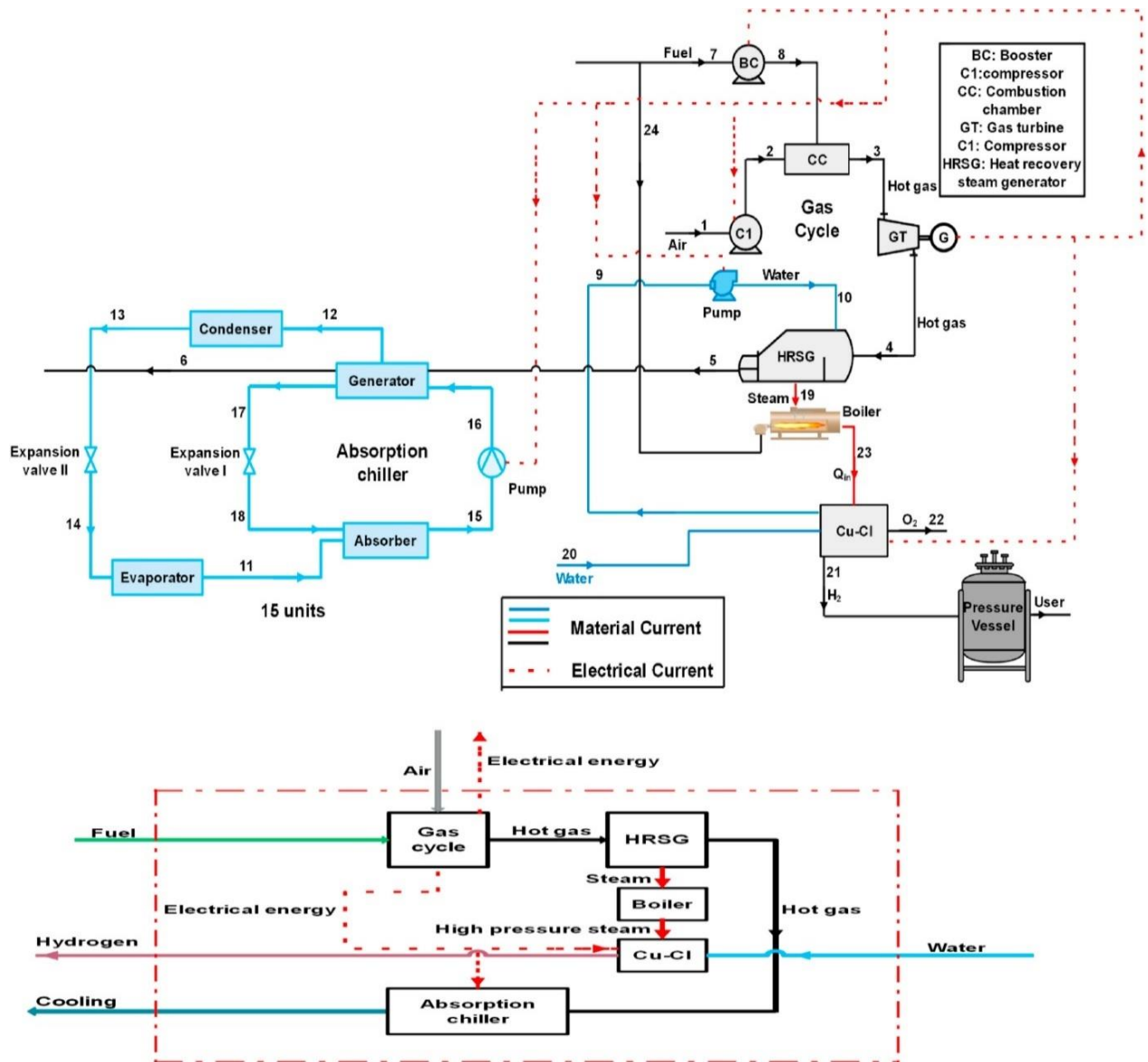


Figure 6. The proposed system configuration of Ref [12]

This proposed system produces 5867.5 kg/h of hydrogen with 735 MW of electricity. The ENE and EXE equations of this triple production system are written as follows [54]:

$$\eta_{\text{energy}} = \frac{\dot{m}_{\text{H}_2} \text{LHV}_{\text{H}_2} + W_{\text{net}}}{\dot{m}_{\text{NG}} \text{LHV}_{\text{NG}}} \quad (46)$$

$$\eta_{\text{exergy}} = \frac{\dot{m}_{\text{H}_2} \text{ex}_{\text{H}_2} + W_{\text{net}}}{\dot{m}_{\text{NG}} \text{ex}_{\text{NG}}} \quad (47)$$

After the mentioned analysis, the proposed system is optimized based on a genetic algorithm. Five scenarios have been considered to optimize this system. In the first to third scenarios, ENE, EXE, and hydrogen-produced price are considered objective functions. In the fourth and fifth scenarios, energy efficiency and price of produced hydrogen and EXE and price of hydrogen are considered objective functions.

In the base state, the ENE and EXE and the price of produced hydrogen are equal to 46.8%, 44.8%, and 4.11 US\$/kg, and using the fifth optimization scenario, these values are equal to 51.7%, 48.2%, and 3.97 US\$/kg.

5. Development policy

5.1 Non-renewable energy resource

For hydrogen production in the Cu-Cl cycle, a heat source with a temperature of about 500 oC and electricity and water are needed. Therefore, the exhaust gases of all kinds of factories that have a temperature higher than 580°C can be a good source for hydrogen production by this cycle. These industries include cement, glass, copper, iron, petrochemicals, etc. The flare exhaust gas of petrochemicals is one of the important sources of energy to achieve this goal. The following options are suggested to supply the consumed electricity for this cycle:

1. Using network electricity if there is an electricity network near the Cu-Cl cycle.
2. Some of the steam produced by the waste hot gases of the industries will be converted into electricity in the steam turbine.
3. If electricity is produced in the factory, the excess consumption of the factory components should be given to the Cu-Cl cycle.
4. If there are renewable energy sources, a power plant should be built to generate electricity from these sources. The produced electricity can be consumed in the Cu-Cl cycle.
5. The oxygen produced by the Cu-Cl cycle can be used as a heat source in cycles that do not require a high-temperature source to produce electricity. These cycles include ORC, Goswami cycle, and Kalina cycle.
6. The remaining energy of the hot gas after supplying the required energy of the Cu-Cl cycle is used in the ORC, Kalina, and Goswami cycles to supply the electricity required for the Cu-Cl cycle.

By comparing the above methods, the best method can be chosen from the point of view of energy, exergy, and economics. Figure 7 shows the schematic of this strategy. It is also reminded that a combination of the above strategies can also be used.

5.2 Renewable energy resource

As mentioned, three factors heat, electricity, and water are needed to produce hydrogen by the Cu-Cl cycle. Naturally, wind, geothermal and water current sources cannot be used to provide the required heat for this cycle, the only renewable energy source that is capable of providing this heat is solar energy. That is if firstly, that region or region has a high potential for solar radiation, and secondly, a heliostat field or PTC should be used to convert this energy into heat. Other types of solar collectors such as flat plates are not suitable for this task due to the limitations of the output fluid temperature. But to provide the electricity required for this cycle, the designer has more options and all types of renewable energy sources can be used provided they have a high potential in that area or region. Figure 8 shows the schematic of this strategy. So, the following options can be considered to produce the electricity required for this cycle:

1. Using network electricity if there is an electricity network near the Cu-Cl cycle.
2. If that area, in addition to the high potential of solar energy, is in the vicinity of geothermal sources, it is possible to convert the energy of the geothermal source into electrical energy in one of the different cycles..., Kalina, ORC, Flash, and from this electricity used in the Cu-Cl cycle.
3. If that area, in addition to the high potential of solar energy, has a suitable wind speed, it is possible to use a wind turbine to produce electricity to provide electricity for the Cu-Cl cycle.
4. The output oxygen of the Cu-Cl cycle can be used in cycles that produce electricity with low-temperature sources (Goswami, Kalina, ORC,...)
5. Some of the steam produced by the PTC and heliostat field will be converted into electricity in a steam turbine

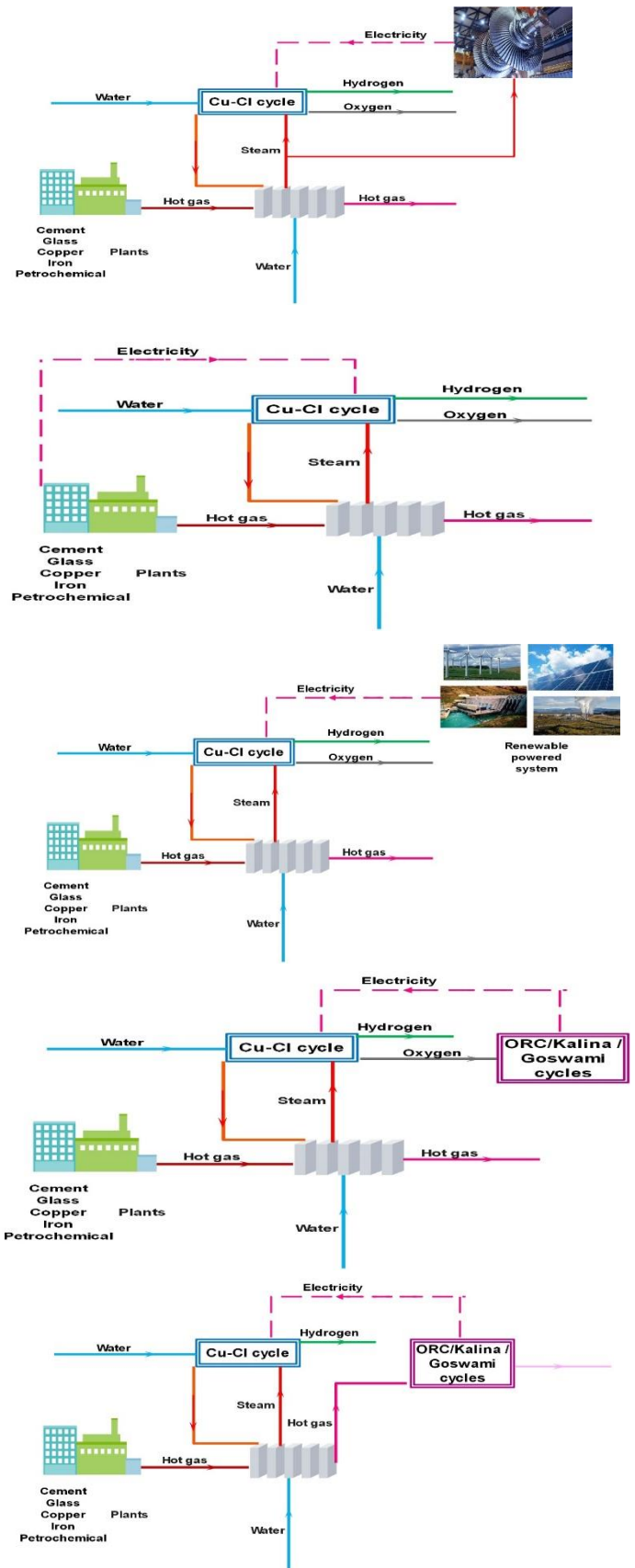


Figure 7. The schematic of the strategy developed for integration of the Cu-Cl cycle with systems powered by non-renewable energy resources (options 1 to 6)

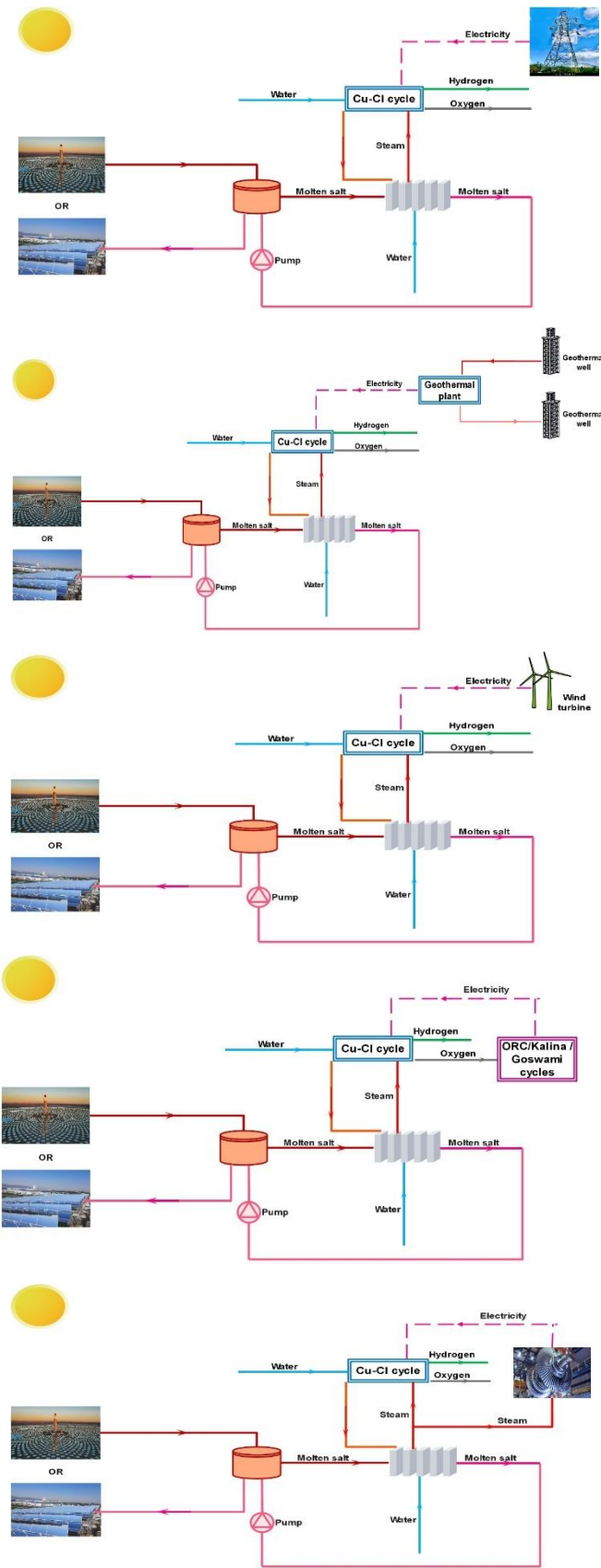


Figure 8. The schematic of the strategy developed for integration of the Cu-Cl cycle with systems powered by renewable energy resources (options 1 to 5)

6. Conclusion

One of the challenges of the current century is the increase in energy demand, the reduction of fossil fuel resources, and environmental problems. Fossil fuels are running out, and due to the destruction of the ozone layer, which has irreparable environmental effects, it is necessary to use suitable alternative fuels such as hydrogen. In addition to having characteristics such as reversibility, storage, and environmental friendliness, hydrogen has a higher calorific value than conventional fossil fuels. There are different methods for hydrogen production, among the thermochemical methods, the Cu-Cl cycle has been expanded and used more due to its relative advantages. According to the heat requirement of this cycle, it is possible to supply the heat needed for this cycle from the waste hot gases of various industries. Therefore, the integration of this cycle with the systems of different industries has economic justification. In general, the requirement of this cycle to produce hydrogen is a heat source with a temperature of 520°C and electricity. To supply electricity to this system, there are different choices of cycles with low source temperature, grid electricity, and power plants with renewable energy sources. Also, to provide heat, the heat needed for this cycle can be used by PTC or HSR, and there are many studies in this field in the research literature, the most important of which are described in this article. The most important results obtained from this research are as follows:

1. It is recommended to use the waste of hot industrial gases for hydrogen production by the Cu-Cl cycle, which can achieve a yield of over 50% due to the efficiency of this cycle and the regenerator heat exchanger.
2. According to the conditions of the system, its size... the PP of the Cu-Cl cycle is about 3 to 4 years if the hot gas heat is recycled, and about 6 to 8 years if the heat is supplied by HSR and PTC.
3. The hot gas discharged after recycling in the Cu-Cl cycle and reducing its temperature can meet the required heat for cycles that work with low-temperature sources (Goswami, ORC, Kalina cycle).
4. The output oxygen of the Cu-Cl cycle can be used as a heat source for cycles that work with low-temperature sources.

Ethical issue

The authors are aware of and comply with best practices in publication ethics, specifically concerning authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests, and compliance with policies on research ethics. The authors adhere to publication requirements that the submitted work is original and has not been published elsewhere in any language.

Data availability statement

Datasets analyzed during the current study are available and can be given following a reasonable request from the corresponding author.

Conflict of interest

The authors declare no potential conflict of interest.

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