

ENERGY INVESTIGATION OF ADVANCED HYDROGEN AND POWER GENERATION SYSTEM BASED ON HYBRID SULFUR AND LITHIUM BROMIDE ABSORPTION POWER CYCLE

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ARTICLE INFO

ABSTRACT

Handling Editor: Rahimah Mahat

Article History:

Received 25 December 2023

Received in revised form 11

January 2024

Accepted 3 February 2024

Available online 15 March 2024

Keywords:

LBr-water absorption power cycle; Hybrid sulfur cycle; Power & hydrogen production; The first law of thermodynamics.

The study aims to improve the solar hybrid sulfur cycle (Shysc) thermal efficiency. The Shysc waste heat is utilized for power generation by integrating the lithium bromide-water absorption power cycle (LiBr-H₂O APC). The developed cogeneration integrated system produces 4.967 moles of hydrogen and 1.22 MW at an efficiency of 60% according to the first law of thermodynamics. The advanced system is 30% more efficient than a conventional hybrid sulfur cycle (Chysc). The efficiency development is due to utilizing the waste heat in the Chysc and converting it into useful power by (LiBr-H₂O APC). Increasing the process's consumed energy harms the system's efficiency. The largest amount of energy is consumed by the thermal cracking process, which reached 69% of the overall energy. Likewise, the electrolyser performance affects the overall efficiency. As the electrolyser performance increases, the amount of converted sulfur dioxide increases and thus, leads to an increase in the amount of produced hydrogen, which enhances the system's efficiency.

1.0 Introduction

Hydrogen, widely acknowledged as a pristine energy carrier of paramount significance, stands as a vanguard among pivotal energy sources [1]. Its combustion yields a noteworthy thermal energy output, measuring 120 MW/kg when considered in the context of its lower heating value. Notably, the chemical interaction between molecular hydrogen (H₂) and oxygen (O₂) exhibits an absence of deleterious emissions, leading exclusively to the formation of water and the liberation of energy. This commendable attribute renders hydrogen a distinguished exemplar of an environmentally conscientious fuel source.

It is imperative to underscore that hydrogen, while not indigenous to the natural environment in an unadulterated form, is prevalently encountered in nature as a constituent of water, wherein it is chemically combined with oxygen. The manifold advantages intrinsic to hydrogen as an energy vector have propelled extensive scholarly inquiry, centering on its synthesis and its potential role as a sustainable alternative to conventional fossil fuels.

The domain of hydrogen production encompasses a spectrum of methodologies, among which the electrochemical process of water electrolysis and the electrochemical reaction involving liquid sulfur dioxide and water within an electrolytic apparatus, commonly referred to as Hysc, is notably prominent [2,3].

In the primary stage of the Hysc process, a solution of sulfuric acid is subjected to thermal treatment, leading to the conversion of sulfuric acid into sulfur trioxide (SO₃) and water. Subsequently, the temperature of the resultant products is elevated, facilitating the transformation of sulfur trioxide gas into oxygen and sulfur dioxide (SO₂), as expounded by the chemical equations denominated in Eq. 1 and Eq. 2. The aqueous solution containing sulfur dioxide is then channelled to the electrolytic cell, where it engages in a transformative interaction with water, ultimately yielding hydrogen, as articulated by Eq. 3. The penultimate phase within this cyclic process involves the concentration of the acid solution, a crucial endeavor in the aftermath of the electrochemical analysis process [4, 5].



Numerous scholarly investigations have made substantial contributions to the progressive evolution of the (HyS). Recent inquiries have advanced our understanding, affirming that the thermal efficiency of the HyS cycle can now attain remarkable levels, within the range of 30-35% [6, 7]. It is imperative to emphasize that the production process of the HyS cycle necessitates a high-temperature energy source, typically surpassing 1000 Kelvin, thereby prompting the utilization of nuclear energy as a prominent energy source [8, 9]. However, in a notable contemporary development, the evolution of solar collector technology has reached a juncture where these collectors can provide thermal energy surpassing 1000 Kelvin. Consequently, solar energy has emerged as a viable alternative for powering the HyS cycle [10-12]. Notably, in the context of solar hydrogen production, recent studies have demonstrated the feasibility of converting solar energy into hydrogen at a commendable conversion efficiency of approximately 10% [7, 13].

The (LiBr-H₂O APC) is a pivotal technological solution employed for the conversion of low-temperature thermal energy into electrical power, as documented by relevant literature [14]. This specialized cycle, which has been systematically developed, extends its utility beyond

power generation to encompass the efficient extraction of cold energy. It accomplishes this dual objective by harnessing a variety of low-temperature energy sources, including but not limited to geothermal energy, various renewable energy sources, and waste heat [15, 16].

The distinguished work of Alperen et al. has significantly contributed to the maturation of the LiBr-H₂O APC. Their innovation centers on the incorporation of a water condenser, a development that serves to enhance the volume of water vapor entering the turbine. This augmentation, in turn, leads to a substantial increase in power production [17]. Additionally, the cycle has witnessed further refinements through the integration of a two-phase ejector at the absorber inlet. This enhancement plays a pivotal role in lowering the absorber's pressure, thereby affecting an overall enhancement of cycle efficiency[18].

Notably, prior research has harnessed the electrical energy generated by the LiBr-H₂O APC to operate an electrolyzed for hydrogen production. Following our previous study, the investigation delineates the possibility of generating 1.15 kilograms of hydrogen, thereby demonstrating varying efficiencies of 6% and 18%. These efficiencies have been rigorously assessed in conformity with the foundational tenets of the first and second laws of thermodynamics. The cost associated with this hydrogen production does not exceed 2.43 US dollars per kilogram, as elucidated in our research findings [19].

In recent developments, solar collectors have undergone significant enhancements, incorporating the innovative use of sand as a thermal energy storage medium. These advancements have propelled the operational temperature of solar collectors to levels exceeding 1000 Kelvin, as substantiated by pertinent scholarly studies [20, 21]. This noteworthy achievement has laid the foundation for effectively harnessing solar energy to fulfil high-temperature energy demands, including applications within the context of the hybrid sulfur cycle [7, 22]. These advancements augur the potential for solar energy to emerge as a compelling alternative to conventional fossil fuels in high-temperature industrial processes.

Drawing upon the technological progress, the present study has leveraged the waste heat energy generated by the cycle, underscoring the feasibility of integrating the Absorption Power Cycle (APC) for the simultaneous production of hydrogen and electrical power. This integrated approach signifies a significant stride toward harnessing renewable energy sources, optimizing energy utilization, and promoting sustainable energy conversion technologies.

2.0 Process Flow Sheet Diagram

The developed hybrid sulfur cycle is summarized in five main processes: Solution concentration, thermal cracking, oxygen separation, electrochemical reaction, and power generation process, which is demonstrated in Figure 1.

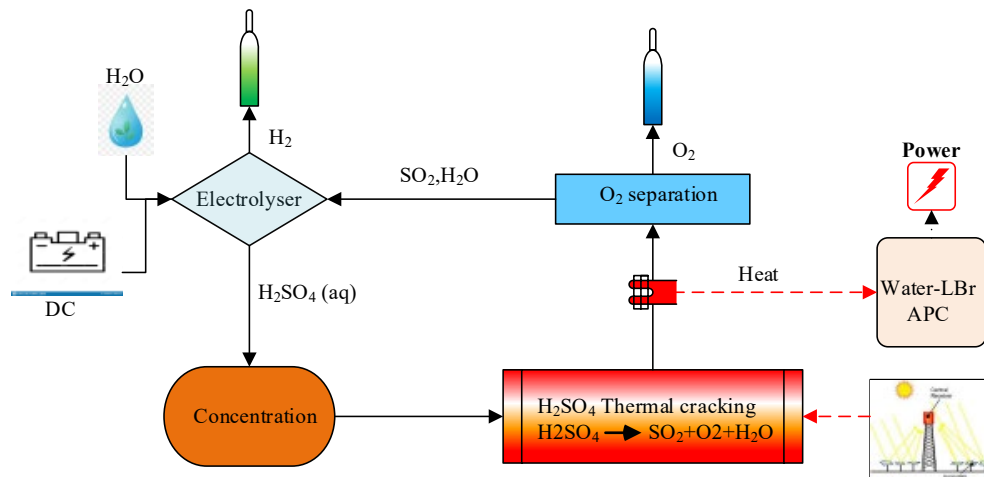


Figure 1. Schematic diagram of advanced (Hysc)-(LiBr-H₂O APC) system

In more detail, Attachment 1&2 presents the finer details of the advanced (Hysc)-(LiBr-H₂O APC). The energy and hydrogen production processes in the advanced system begin with the thermally concentrating of solution (1-2). The temperature of the concentrated sulfuric acid solution is raised in the superheater to evaporate, and thus the acid decomposes into SO₂ and water (4-6). The temperature of the steam in the decomposer is raised to a temperature (1520K) at which most of the SO₃ converts to SO₂ and O₂ (6-7). The thermal energy of the steam is recovered through a series of 3 heat exchangers (7-10). The temperature of the steam drops, causing a little condensation, and converting the remaining sulfur SO₃ to acid (10). SO₂ is separated, and the liquid, consisting mostly of an acid solution, is sent to the mixing tank (10B). The gas, which consists mostly of (SO₂) is cooled to turn into a mixture phase before raising the pressure to the absorber pressure (12A). The gas pressure is raised to the absorber pressure (12 bar) in two stages (11-12) and then (13-15). The heat generated as a result of gas pressurized is recovered (16) and (13). The liquid gas pressure is lifted directly to the absorber pressure (12B-17). At the absorber inlet, the mixture is cooled to 313K and the O₂ is then separated and collected as an additional cycle product (17-O₂). The liquid is heated downstream of the absorber through the heat exchanger (18-20). The mixture enters distillation device 1, and excess water is separated and recycled to the absorber (21A-21B).

SO₂ enters the electrolyser at the liquid phase and reacts with water to produce hydrogen. In addition to hydrogen, the reaction produces sulfuric acid and heat, which contributes to raising the temperature to 370 K. Because of this, the analyser does not need external heat.

The study assumes that 40% of the SO₂ reacts to produce hydrogen. The mixture coming out of the electrolyser containing the residual (SO₂) is heated before being fed into the distiller 2 (25-26). The distillate residual gas is sent back to the electrolyser (29-23). As for the acidic solution, it is sent to the tank after recovering part of its energy (27-28), thus completing the hybrid cycle.

The (LiBr-H₂O) cycle is operated by heat recovered from the hybrid cycle. Two absorption cycles are integrated to utilize the recovered energy as much as possible. The (LiBr-H₂O) cycle begins by raising the temperature of the weak lithium bromide solution in the heat exchangers so that part of it is evaporated (30) and (39A&B). Water vapor is separated and enters the turbine to generate power (31) and (40). The energy of the concentrated solution is recovered by the heat exchangers, and the mixture is then cooled in the absorber where the absorption process takes place (32-35) and (42-48). The saturated solution pressure and temperature are

raised by the pump and heat exchangers respectively, thus completing the cycle (37-30) and (49-39A&B).

DWSIM was utilized to simulate the process and generate material and mass, energy balance. DWSIM is an open-source, chemical process simulator compliant with computer-aided process engineering (CAPE) [23].

3.0 Result and Discussion

The advanced system consumes 4031.45 kW of energy to produce 4.96 moles of hydrogen and 1.22W. Each stage of the system consumes a portion of energy, directly affecting the system's efficiency. To determine the effect of each stage on the overall efficiency, the amount of consumed energy in each stage is calculated, and its impact on the overall efficiency is studied.

3.1 Process Energy Demand

The energy consumed by each process and the parameters affecting it are calculated and studied. As well as studying its impact on the overall system's efficiency.

3.1.1 Solution Concentration Process

Hydrogen production processes in the hybrid cycle begin with the concentration process. The required acid concentration for the process is 62%, which requires heating the solution to 380,504 K, consuming an energy of 4.73 kJ/mol H₂, which represents 0.582% of the total energy.

3.1.2 Sulfuric Acid Thermal Cracking

The main purpose of the process is SO₂ production. The process occurs at 1520K and consumes a thermal energy of 565.86 kJ / mol hydrogen, which is 69.613% of the overall energy. Fig.2 demonstrates the effect of decomposer temperature on the SO₃ conversion rate. As the figure shows, the rate increases with increasing the decomposer temperature. At 1573 most of the SO₃ gas converts into SO₂.

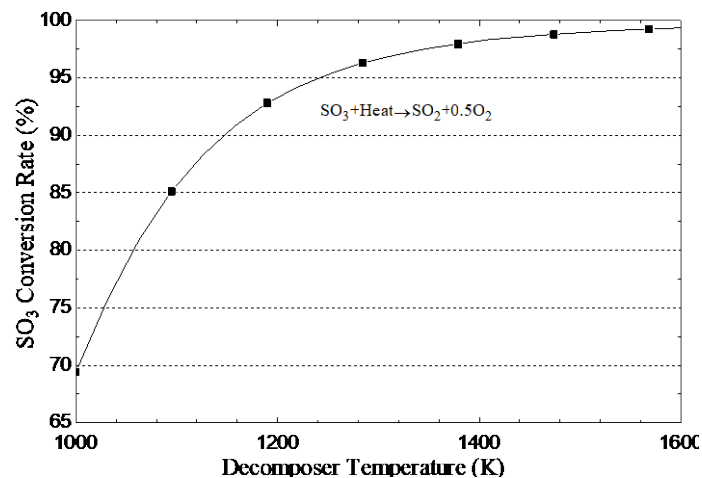


Figure 2. SO₃ conversion rate

3.1.3 Gas compression process

The pressure of the thermal cracking products is lifting to the absorption pressure of 12 bar. Pressure lifting equipment consumes an energy of 18.59 kJ/mole, which constitutes 2.287% of the total energy.

3.1.4 Oxygen Separation Process

O₂ is separated through two stages. The beginning stage is absorbing SO₂ by water (SO₂ aqueous). O₂ remains only at the gas phase to be separated and collected. Figure 3 demonstrates the effect of the O₂ mass fraction on the absorbed SO₂. As the O₂ mass increases in the mixture, the amount of absorbed SO₂ decreases. As for the water fraction in the mixture, it has a positive effect on the absorption process. In contrast to the first stage (absorption), the SO₂ distillation consumes thermal energy of 61.65 kJ/mol (H₂) which equals 7.59% of the system's energy. Figures 4a and b show the effect of the amount and temperature of the water on the consumed energy, as well as on the distillation temperature. The distillation energy (column 1) decreases with the increase in the inlet water temperature, while the distillation temperature is almost steady. Figure 4b demonstrates that distillation energy increases with increasing water mass fraction. The more water there is, the more heat is needed to heat it and separate the SO₂. Because of this, the excess water should be avoided. In addition, Figure 4b, plots the effect of O₂-SO₂ mass fraction on the distillation energy, the ratio does not greatly affect the energy.

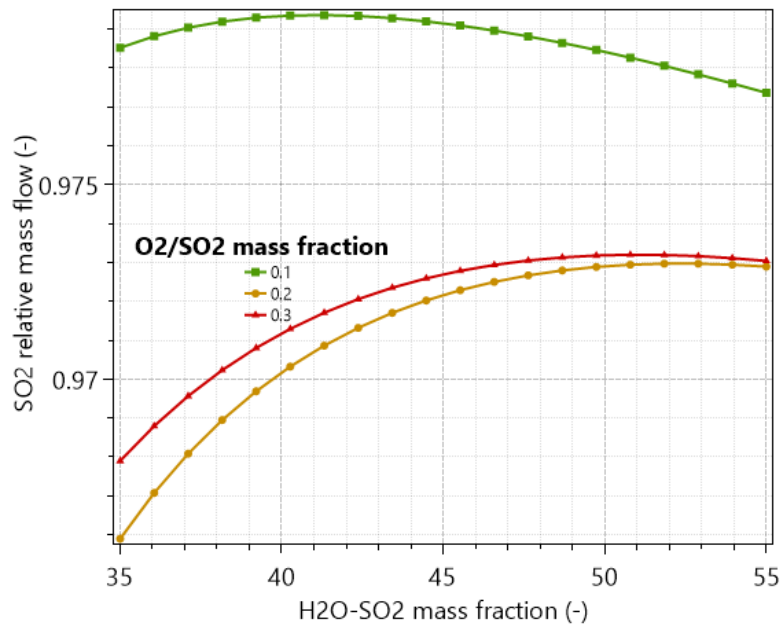


Figure 3. The effect of oxygen and water on the SO₂ solubility

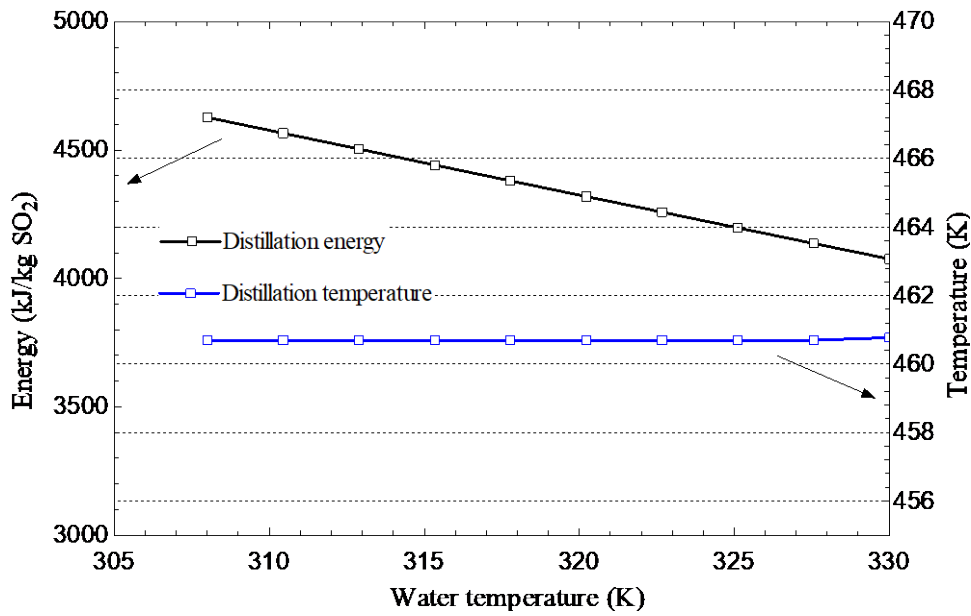


Fig. 4 (a)

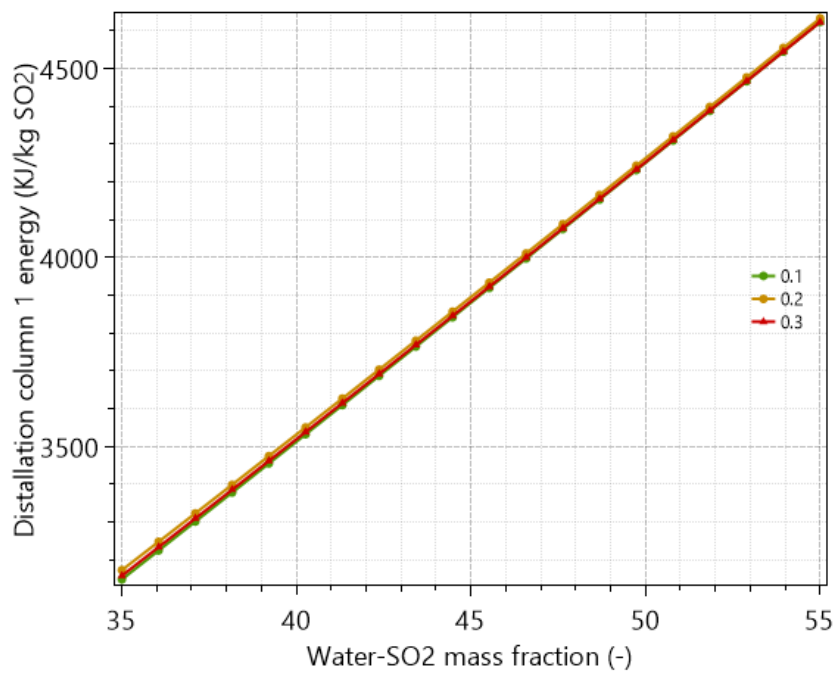


Fig. 4 (b)

Figure 4. Effect of the water temperature (a) and water fraction (b) on the distillation column1 energy.

3.1.5 Electrochemical Hydrogen Generation

4.96 moles of hydrogen are produced using a reversible and operating voltage of 0.158, and 0.6 volts respectively, with an electric power of 115 kJ/mol(H₂) and a current density of 500

mA/cm^2 . 40% of SO_2 reacts with water to produce this amount, consuming 14.148% of the system's total energy.

3.1.6 Distillation of Excess SO_2

The final stage to complete the system cycle is the distillation of SO_2 leaving the electrolyser that has not reacted with water (distillation column 2). It is extracted in distiller 2, consuming an energy of 47 kJ/mol, which constitutes 5.786% of the total energy. The electrolyser performance affects the amount of remaining SO_2 , which in turn affects the amount of energy needed for the distillation. Figure 5 shows that the consumed energy in the distillation device depends on the electrolyser efficiency. By increasing the electrolyser performance, the amount of remaining gas decreases and thus leads to a reduction in the energy. As for the temperature distiller, it is not affected by the electrolyser performance.

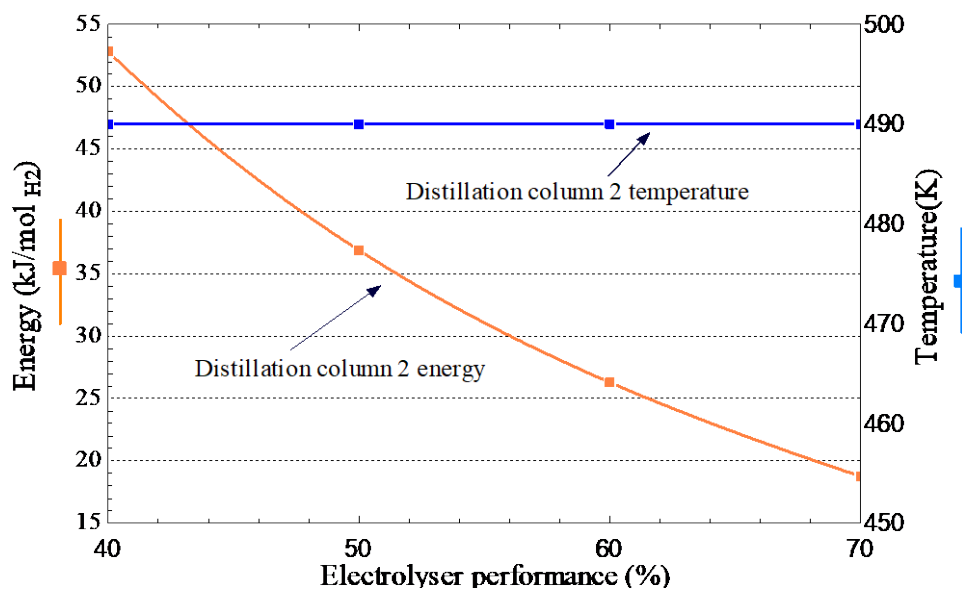


Figure 5. Effect of electrolyser performance on the distillation column2 energy.

Figure 6 studies the effect of water mass fraction on distillater2 energy and distillation temperature. Increasing the water mass fraction increases the distillation energy because the energy is consumed for heating and evaporating the excess water. While the distillation temperature decreases, due to the increase in the proportion of solvent.

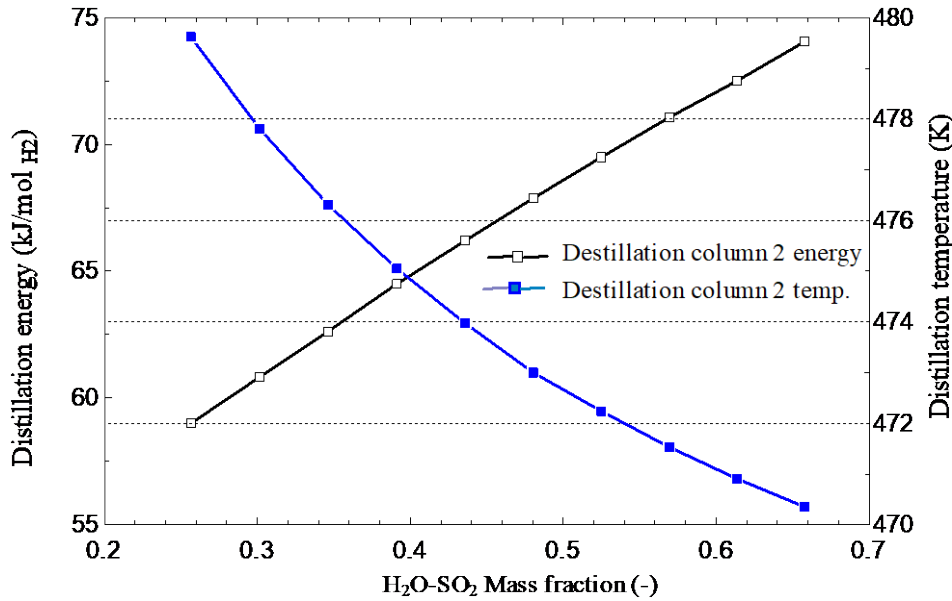


Figure 6. Effect of water fraction on distillation column2 energy.

4.0 System Energy Efficiency

The efficiency of any thermodynamic system is the percentage of the gained energy to the expended energy. The process energy efficiency of a conventional hybrid cycle which only produces hydrogen is 30% based on the hydrogen low value, which is consistent with most previous studies. By integrating the absorption power cycle and utilizing the heat recovery, an additional 0.246 MJ/mol(H₂) is produced, causing an increase in the total efficiency of the system to approximately 60%.

The system efficiency is affected by the decomposer temperature. Figure 7 shows the efficiency curve of the conventional hybrid cycle, as well as the curve of the advanced system. The optimum value of efficiency is achieved at 1520 K.

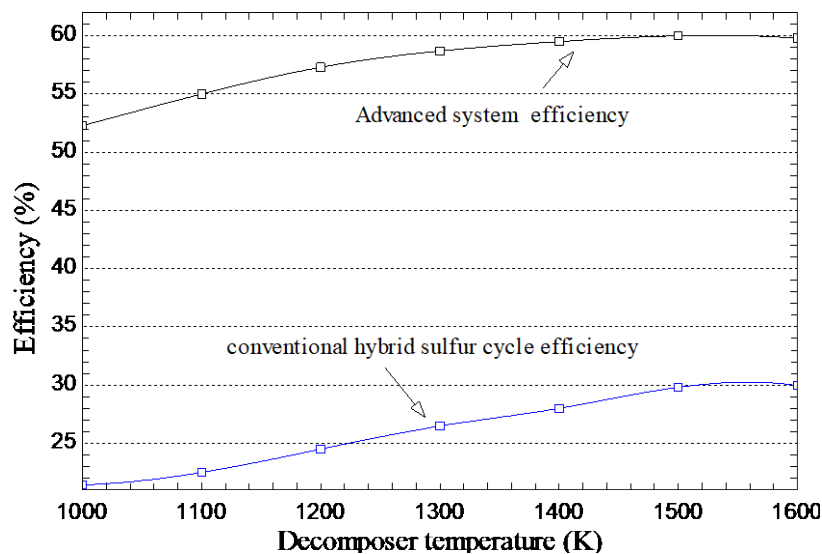


Figure 7. Effect of the decomposer temperature on the system efficiency.

5.0 Conclusions and Outlook

1. The system under examination has demonstrated the production of 1.22 MW of power and the generation of 4.97 moles/s of hydrogen. This power production was achieved with a total energy consumption of 4031.45 kW, resulting in a commendable thermal efficiency of 60%.
2. It is noteworthy that a substantial portion of the total energy consumption, specifically 69%, is consumed by the thermal cracking process. This insight underscores the significance of addressing the energy demands associated with this particular step
3. Further investigation reveals that an increase in the oxygen mass fraction within the absorber has the effect of reducing the rate at which gas is dissolved in the water. Consequently, a higher energy input is required to achieve the desired results.
4. Conversely, the presence of excess water within the absorber also imposes a greater energy demand, emphasizing the importance of minimizing excess water.
5. Notably, improvements in electrolyser performance yield a dual benefit: a reduction in energy consumption and an increase in hydrogen production. This, in turn, contributes to an overall enhancement in the system's efficiency.

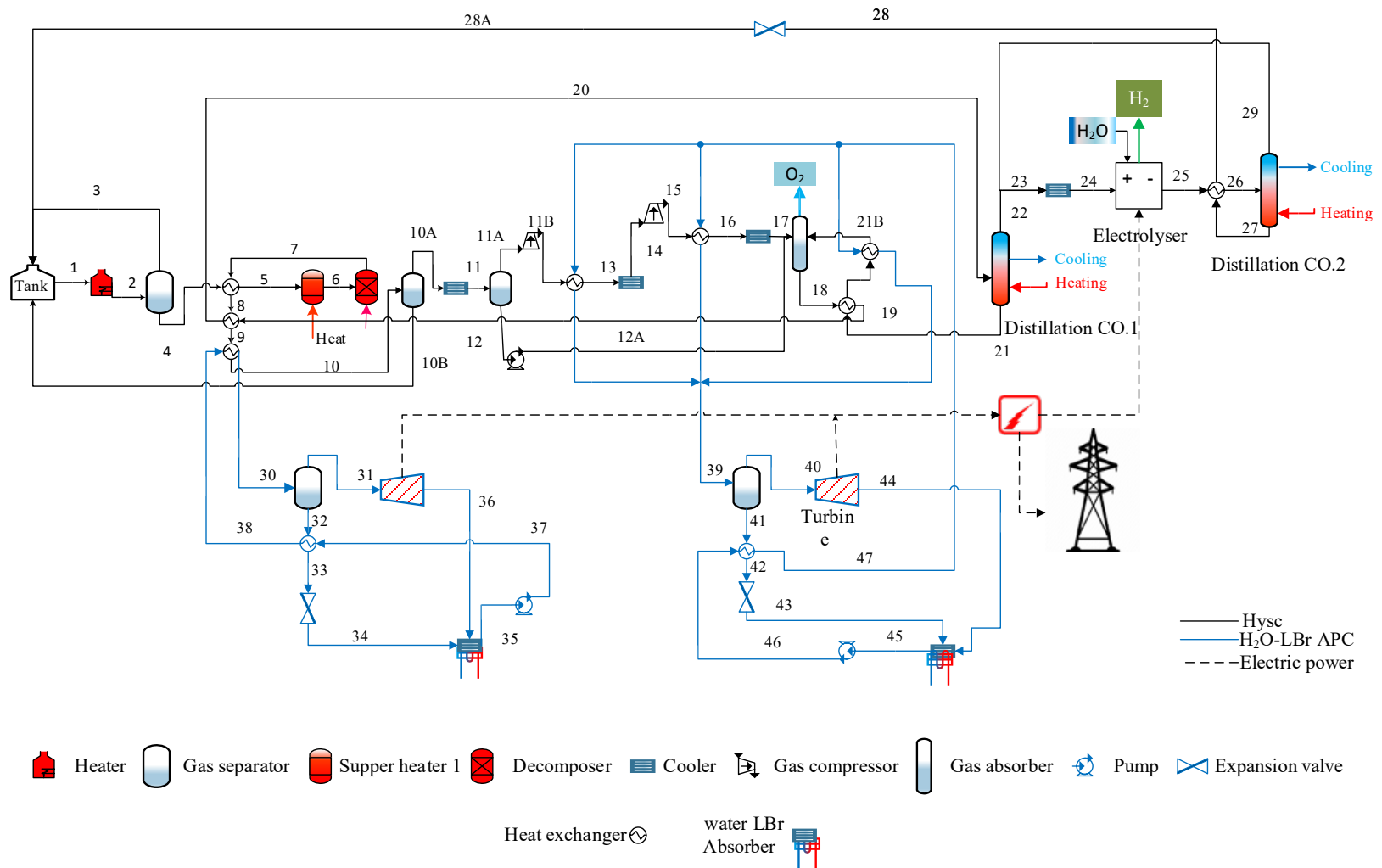
In light of these findings, there is potential for future studies to explore the integration and evaluation of the Hybrid Sulphur Cycle (HyS) with a power cycle that exhibits superior thermal efficiency in comparison to the water-LiBr absorption cycle. Additionally, the system's efficiency can be further augmented by capitalizing on waste heat for various auxiliary purposes, including water desalination and heating. These avenues for improvement hold promise in the pursuit of more efficient and sustainable energy systems.

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Attachment 1. Advanced System flow diagram



Attachment 2. Advanced system process streams statement

Stream (No)	Pressure (bar)	Temperature (K)	Mass fraction (-)						Vapure fraction
			H2O	H2SO4	SO3	SO2	O2	H2	
1	1	381.3	0.503	0.497	0	0	0	0	0.3
2	1	381.5	0.503	0.497	0	0	0	0	0.34
3	1	381.5	0.98	0.02	0	0	0	0	1
4	1	381.5	0.38	0.62	0	0	0	0	0
5	1	419	0.38	0.62	0	0	0	0	0.91
6	1	673	0.49	0	0.51	0	0	0	1
7	1	1520	0.49	0	0.005	0.4	0.1	0	1
8	1	702	0.49	0	0.005	0.4	0.1	0	1
9	1	457	0.49	0	0.005	0.4	0.1	0	1
10	1	352	0.49	0.006	0	0.4	0.1	0	1
10A	1	352	0.199	0	0	0.64	0.16	0	1
10B	1	352	0.984	0.016	0	0	0	0	0
11	1	313	0.199	0	0	0.64	0.16	0	0.616
11A	1	313	0.023	0	0	0.782	0.195	0	1
11B	4	460	0.023	0	0	0.782	0.195	0	1
12	1	313	0.999	0.001	0	0	0	0	0
12A	12	313.1	0.999	0.001	0	0	0	0	0
13	4	348	0.023	0	0	0.782	0.195	0	1
14	4	340	0.023	0	0	0.782	0.195	0	1
15	12	462	0.023	0	0	0.782	0.195	0	1
16	12	347.78	0.023	0	0	0.782	0.195	0	0.967
17	12	313	0.023	0	0	0.782	0.195	0	0.612
18	12	345	0.936	0	0	0.064	0	0	0
O ₂	12	308	0	0	0	0	1	0	1
19	12	459.5	0.936	0	0	0.064	0	0	0.52
20	12	460	0.936	0	0	0.064	0	0	0.86
21	12	461.2	1	0	0	0	0	0	0.867
22	12	342.7	0.934	0	0	0.046	0	0	0.002
23	12	339	0.0278	0	0	0.9722	0	0	0
24	12	313	0.0278	0	0	0.9722	0	0	0
25	12	378	0.026	0.39	0	0.584	0	0	0.58
H ₂	12	378	0	0	0	0	0	1	1
26	12	446.88	0.026	0.39	0	0.584	0	0	0.653
27	12	502.7	0.01	0.99	0	0	0	0	0
28	12	380	0.01	0.99	0	0	0	0	0
28A	1	380	0.01	0.99	0	0	0	0	0
29	12	336	0.002	0	0	0.998	0	0	0.004

LiBr-H₂O APC 1 process streams statement

Stream (No)	Pressure (bar)	Temperature (K)	Mass fraction(-)		Vapour fraction (-)
			H2O	LiBr	
30	14.5	441	0.33	0.67	0.69
31	14.5	441	1	0	1
32	14.5	441	0.006	0.994	0
33	14.5	326	0.006	0.994	0
34	0.144	326	0.006	0.994	0
35	0.144	308	0.33	0.67	0
36	0.144	326	1	0	0.89
37	14.5	308.4	0.33	0.67	0
38	14.5	350	0.33	0.67	0

LiBr-H₂O APC 2 process streams statement

Stream (No)	Pressure (bar)	Temperature (K)	Mass fraction (-)		Vapour fraction (-)
			H2O	LiBr	
39	18	447	0.33	0.67	0.69
40	18	447	1	0	1
41	18	447	0.006	0.994	0
42	18	341	0.006	0.994	0
43	0.144	341	0.006	0.994	0
44	0.144	326	1	0	0.81
45	0.144	308	0.33	0.67	0
46	18	308.47	0.33	0.67	0
47	18	346	0.33	0.67	0