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Investigation of a Novel Net-Zero Polygeneration System for Power, Hydrogen and Ammonia Production

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ABSTRACT

This study investigates a novel net-zero polygeneration system for the production of power, hydrogen, and ammonia. The integration of oxy-combustion, an alkaline electrolyzer, and ammonia synthesis via the Haber-Bosch process significantly enhances the efficiency of individual components and the overall system showcasing its potential for developing more sustainable and efficient energy solutions.

Keywords: polygeneration system, power production, hydrogen, ammonia, process simulation

NONMENCLATURE

Abbreviations	
ASU	Air Separation Unit
NZC	Net Zero Cycle
ACM	Aspen Custom Modeler
FC	Fractional conversion
Symbols	
$\dot{m}$	Mass flowrate
$\dot{W}$	Power

1. INTRODUCTION

Anthropogenic CO_2 emissions from the power, hydrogen, and ammonia production industries have significantly contributed to climate change, underscoring the urgent need for sustainable production methods [1, 2]. In power production sector, oxy-combustion utilizes nearly pure oxygen, obtained through an air separation unit (ASU), allowing for easier separation of CO_2 from effluent and achieving net-zero CO_2 emissions [3]. Allam Cycle, also referred as NZC (Net Zero Cycle), shows the highest efficiency of the power production among other methods of the power production [4]. Hydrogen serves as both an energy carrier and a vital feedstock for various processes, including ammonia production [1]. It is notable for its high energy density and zero-emission potential when produced from renewable resources, making it an essential component of sustainable energy systems [5]. Currently, the majority of hydrogen production is obtained through Steam Methane Reforming (SMR), which generates what is termed "gray hydrogen." This process emits significant amounts of CO_2 into the atmosphere, contributing to environmental damage [6, 7]. As a result, utilizing renewable resources to produce green hydrogen should be considered to reach sustainable hydrogen production. Alkaline electrolyzes utilizing renewable resources are known for their reliable performance, high efficiency, quick dynamic response, and ability to produce green hydrogen with satisfactory purity [8]. In addition, ammonia holds great promise for a low-carbon future, with a volumetric energy density of 12.7 MJ/L—three times higher than compressed hydrogen at 69 MPa and 25°C, and about ten times greater than lithium-based batteries [9]. Ammonia production is essential for the fertilizer industry and is also recognized as an efficient energy carrier and fuel [10]. Polygeneration processes, which produce electricity, heat, and chemicals simultaneously, boost resource efficiency and reduce environmental impact by integrating energy systems, resulting in lower emissions and resource use [11]. This study explores the integration of oxy-combustion, hydrogen, and ammonia production, demonstrating the potential for developing more efficient and sustainable energy systems. Both the individual processes and the overall integrated system are studied.

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2. MATERIAL AND METHODS

Fig. 1 illustrates the proposed polygeneration system for producing power, hydrogen, and ammonia. The study utilized the process simulator Aspen Plus V.14, licensed by Aspen Tech. Alkaline electrolyzer was modeled in Aspen Custom Modeler (ACM) according to [12-14] study, and imported to Aspen Plus while other unit operations were simulated with Aspen Plus in-built unit operations. Alkaline electrolyzers are typically operated at temperatures between 70 and 140°C, with pressures ranging from 15 to 30 bar, using an aqueous KOH solution at a concentration of 25-35 wt% [15, 16].

NZC is favored for oxy-combustion power generation, as it is widely regarded as the most efficient method for producing power in such processes [17]. The combustor is modeled using an RGibbs reactor with 3% excess O_2, and the combustion temperature is regulated by the recycling streams. The 15-stage cooled turbine is modeled based on El-Masri’s continuous expansion model [4]. The regenerators are modeled as multi-stream heat exchangers, with a minimum temperature difference of 20°C in the "Top regenerator" and 5°C in the "Bottom regenerator”. Additionally, temperature crossover is monitored by dividing both regenerators into 50 zones. An air separation unit (ASU), with an energy consumption of 1365 kJ/kg_{O2} [4], is simulated as a black-box model. It supplies part of the oxygen needed for combustion, nitrogen for the ammonia-synthesis process, and provides excess heat to both regenerators. A carbon sequestration unit is integrated into the process to capture a portion of the generated CO_2, proportional to the fuel's mass flow rate, in order to prevent the direct release of CO_2 into the atmosphere. A portion of the electricity generated in the NZC is used to power all the turbomachinery in the system, while the remaining electricity is considered the net power production.

Ammonia is produced through the Haber-Bosch process, combining hydrogen and nitrogen in a 3:1 ratio [18]. Ammonia synthesis is an exothermic reaction [19], and a three-stage cascade process is being explored to enhance system efficiency through effective heat integration. By utilizing the heat generated in each stage, this approach aims to improve overall energy efficiency and performance in ammonia production. The ammonia reactors are modelled using REqiul reactor.

3. THEORY AND CALCULATION

In this study, following assumptions have been made:

1. The system is simulated and analyzed under steady-state conditions.
2. Pressure losses in the system's piping are neglected.
3. The electrolyzer is powered by firmed renewable energy sources.
4. The minimum operating temperature of the system is set to 26°C.

Heat integration promotes process efficiency by optimizing energy use [20]. Considering original NZC system layout [21], the top and bottom regenerators are modified to harness excess heat from the ammonia synthesis and electrolyzer outlet streams. This effective heat utilization minimizes the reliance on cooling utilities in the hydrogen and ammonia production subsystems, enhancing overall efficiency. Moreover, the condensed water from the NZC is already deionized, allowing it to be directly used as feedwater for the electrolyzer, thereby removing the need for a desalination unit. In the stand-alone NZC layout, the primarily role of ASU is to produce oxygen using air, while nitrogen typically being released into the atmosphere. However, with the current system design and integration, the nitrogen generated by the ASU can be redirected into the ammonia synthesis process. This eliminates the need for a distinct ASU unit for large-scale ammonia production or pressure swing adsorption for medium-scale operations. The sizes of these three systems are determined so that no additional O_2 from the electrolyzer and ASU, nor extra N_2 generated by the ASU, remain. Additionally, the net mole flow rates of ammonia and hydrogen production are balanced.

This study employs the first law of thermodynamics to assess the efficiency of individual processes, such as the NZC, hydrogen production, and ammonia production, as well as the overall system efficiency. The overall efficiency of the polygeneration system is calculated using following equation:

$$\eta_{Poly_{sys}} = \frac{(\dot{W}_{gross,turb.} - \dot{W}_{comp.}) + \dot{m}_{H_2,net}.LHV_{H_2} + \dot{m}_{NH_3}.LHV_{NH_3}}{\dot{m}_{fuel}LHV + \dot{W}_{elec.}} \quad (1)$$

In this context, $\dot{\mathrm{W}}_{\mathrm{gross,turb.}}$ indicates the gross power output produced by the turbine, whereas $\dot{\mathrm{W}}_{\mathrm{comp.}}$

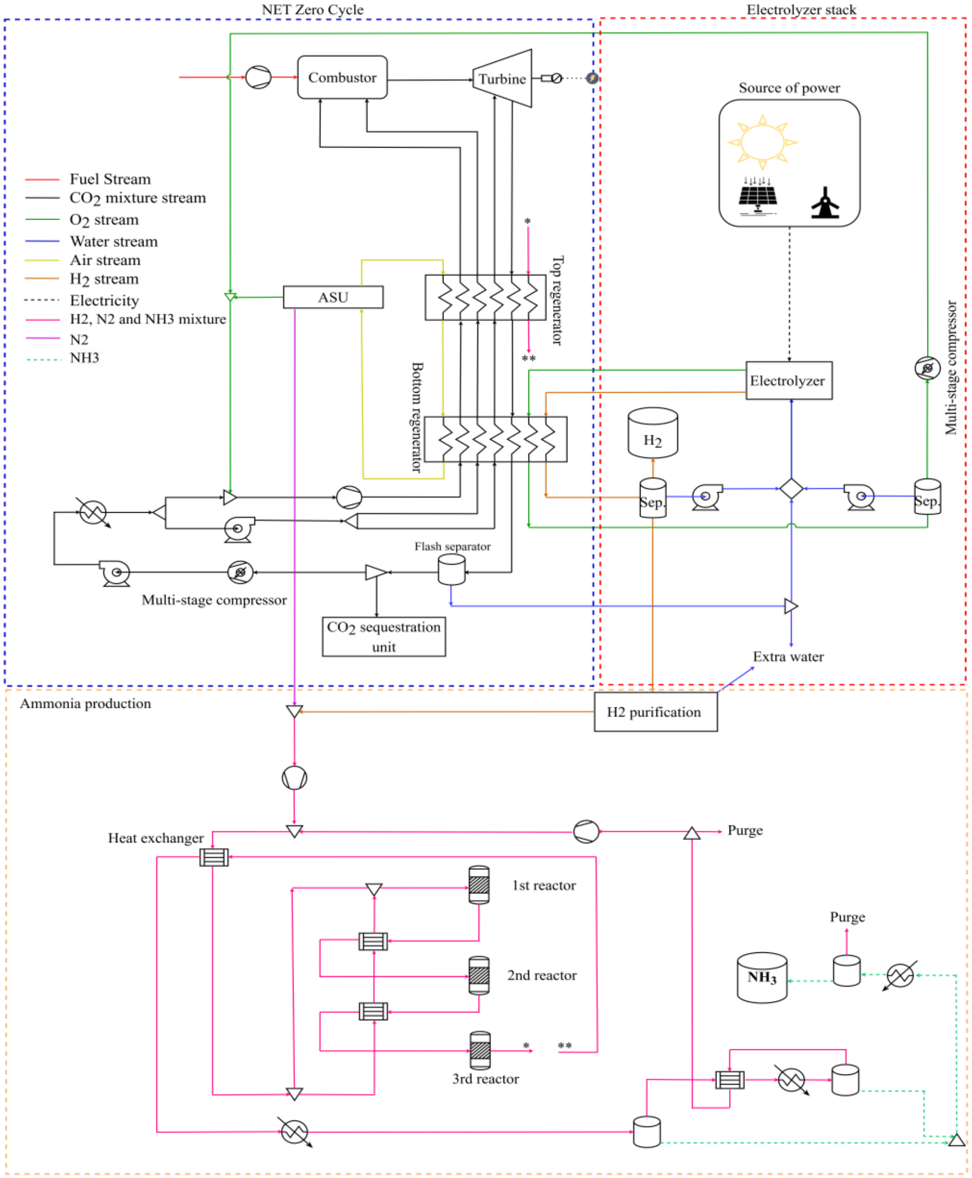

Fig. 1 Layout of the proposed polygeneration system for power, hydrogen, and ammonia production

signifies the total energy consumption of the turbomachinery within the system. The term $\dot{m}$ represents mass flow, LHV stands for the lower heating value, and $\dot{W}_{elec.}$ refers to the renewable energy input used to operate the electrolyzer.

4. RESULTS AND DISCUSSION

Table 1 presents the outcomes of the polygeneration system. As shown, the NZC achieves an efficiency of 66.1%, which is considerably higher than the 54% efficiency of the standalone NZC under the same operating conditions, as reported in [4] study. The environmental benefit of this improved efficiency means that more electricity is generated without increasing CO_2 emissions, as CO_2 capture remains constant. The condensed water from the NZC subsystem exceeds the amount needed to fully meet the deionized water requirements of the electrolyzer. The ammonia production efficiency is 77.2%, with a purity of 99.9%. During the ammonia synthesis process, the single-pass fractional conversion of hydrogen in the 1st, 2nd, and 3rd reactors is 20.2%, 15.9%, and 12.7%, respectively. However, by recycling the unreacted components and employing effective heat integration, the ammonia yield increases to 96.2%. This yield surpasses the 94.2% yield reported by [10] study for ammonia production in the polygeneration system. Additionally, the high purity of hydrogen and nitrogen fed into the ammonia process contributes to this elevated yield. Finally, the overall system demonstrates an efficiency of 62.2%. This efficiency should be compared with other polygeneration systems that produce ammonia.

Table 1 Polygeneration system results

Properties	Unit	Polygeneration system
Thermal energy of fuel (LHV)	MW_{th}	768.3
Renewable energy input	MW_e	1186.1
Combustor temperature	°C	1100
Combustor pressure	bar	300
Turbine outlet pressure	bar	34
Turbine power output	MW_e	650.9
Recycle flow energy consumption	MW_e	178.91
NG compressor	MW_e	4.3
Air separation unit	MW_e	8.7
NZC net electric power output	MW_e	507.9
Overall system net power output	MW_e	463.3
Gross hydrogen production rate	kmol/s	3.44
Net hydrogen production rate	kmol/s	1.34
Ammonia production rate	kmol/s	1.34
Hydrogen FC in 1st reactor	%	20.2
Hydrogen FC in 2nd reactor	%	15.9
Hydrogen FC in 3rd reactor	%	12.7
Purity of ammonia production	mole%	99.9
Ammonia production yield	%	96.2
Electrolyzer efficiency (LHV)	%	70.2
NZC efficiency (LHV)	%	66.1
Ammonia production efficiency (LHV)	%	77.2
Overall system efficiency (LHV)	%	62.2

5. CONCLUSION

Integrating the NZC, alkaline electrolyzer, and ammonia production via the Haber-Bosch process not only enhances the standalone efficiency of the NZC and boosts ammonia yield but also results in a highly efficient overall system. This integration increases NZC power production efficiency from 54% to 66.1%. Hydrogen and ammonia can be produced with efficiencies of 70.2% and 77.2%, respectively. From an environmental perspective, this process results in zero direct CO_2 emissions into the atmosphere, and the deionized water produced by the NZC subsystem completely eliminates the need for a desalination unit.

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