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Hydrogen Production from Low-Grade Agricultural Waste: Integrated Drying, Gasification, and Chemical Looping

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Chemical looping hydrogen production (CLH$_2$) is a new technology used to produce H_2 from fuel while separating CO_2 simultaneously. Rice husk is considered as a promising energy source in the future because of its high energy potential and carbon neutral characteristics, although currently it is not being used effectively. This research aims to build an integrated conversion system of rice husks to H_2 with high energy efficiency. The developed system mainly consists of superheated steam drying, steam gasification, syngas chemical looping, and Haber-Bosch process. To enhance the efficiency, exergy recovery and process integration technologies are adopted. Fe_2O_3 and Al_2O_3 are used as oxygen carrier and heat carrier for CLH$_2$. The energy efficiency is evaluated using Aspen Plus. The effect of chemical looping temperature, and the effect of recycle to feed stream ratio for NH_3 synthesis were selected for the parameters and evaluated. The highest NH_3 efficiency achieved through the simulation was 5.77 % and the power efficiency was 1.96 %.

1. Introduction

Hydrogen (H_2) is considered as a promising candidate to replace fossil fuels in the future because of its high efficiency, carbon-free characteristics, high flexibility in its production and utilization, and has the potential to solve some environmental problems. Among many sources to produce H_2, biomass is receiving high attention due to its advantages, including carbon neutral characteristics, large energy potential, and low cost. As one of biomass, rice husk also has high energy potential. Every year, the total amount of produced rice husk around the world is about 120 Mt (Lay et al., 2020). From both economic and environmental points of view, it is necessary to develop an efficient conversion system of H_2 from rice husks.

Darmawan et al. (2018) proposed an integrated system of rice production and power generation and achieved an electricity production efficiency of about 32 %. Superheated steam drying (SSD) was used to dry the paddy in the parboiling process, which is a pretreatment process for rice grains. SSD was selected because it could realize higher drying rate, better quality, and lower net energy consumption compared to other drying methods. However, they only focused on the conversion of rice husk to power and lacked consideration about the possible conversion to H_2, which is also an important aspect for broader utilization.

The conventional H_2 production method, which is steam methane reforming, is a complex process including water gas shift and pressure swing adsorption units, making the total energy conversion efficiency to be low. Recently, chemical looping H_2 production (CLH$_2$) technology is receiving intensive attention due to its free-carbon characteristics and high conversion efficiency (Fernández and Abanades, 2016).

Although H_2 has advantageous characteristics, its volumetric energy density is very low (only about 3 Wh/L). Hence, more efficient H_2 storage, both gravimetric and volumetric H_2 densities, is urgently demanded. Among many H_2 storage technologies, NH_3 is a preferred option because of its high storage capacity, applicability, economic performance, and H_2 density. Haber-Bosch process, the main process for NH_3 production, utilizes purified N_2 and H_2 and reacts them under high temperature (400–550 °C) and high pressure (up to 30 MPa) condition, which is highly energy consuming. Nurdiawati et al. (2019) proposed an integrated system of CLH$_2$ and NH_3 synthesis by utilizing the H_2-rich gas from the oxidizer and N_2-rich gas from the combustor and achieved a high total energy efficiency of up to 64.3 % and showed high affinity between CLH$_2$ and NH_3 synthesis. However, this research focused on microalgae, not the rice industry.

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To our best of knowledge by searching in Google Scholar database, there is almost no study which effectively combine rice production procedure with CLH_2 and NH_3 production, especially on improving the energy efficiency. In this study, a new integrated system of rice SSD, husking, steam gasification, syngas CLH_2, and Haber-Bosch process is proposed. This research aims to achieve high energy efficiency by minimizing the exergy loss through exergy recovery and process integration.

2. Proposed integrated system

The proposed system consists of five process modules including SSD, husking and polishing, steam gasification, syngas CLH_2, and NH_3 synthesis employing Haber-Bosch process. Figure 1 shows the schematic flow diagram of the material and electricity in the integrated system. The harvested rice grain goes to the parboiling process where it is steamed and dried through SSD. The dried rice grain flows to the husking process where rice husk is separated. The separated rice husk then goes to the steam gasification where it is converted to syngas, and the produced syngas is fed to the CLH_2 module to produce H_2 while separating CO_2. CLH_2 module consists of three circulated reactors, including reduction, oxidation, and combustion reactors. The produced H_2-rich gas from the oxidizer is either pressurized and used to run fuel cell-based agricultural machines (such as forklift and tractor) or mixed and reacted with N_2-rich gas from the combustor to produce NH_3 through Haber-Bosch process. In case of the latter, the produced NH3 can be utilized whether as agricultural fertilizer or fuel. The integrated system is considered able to realize a new circular economy in agricultural sector.

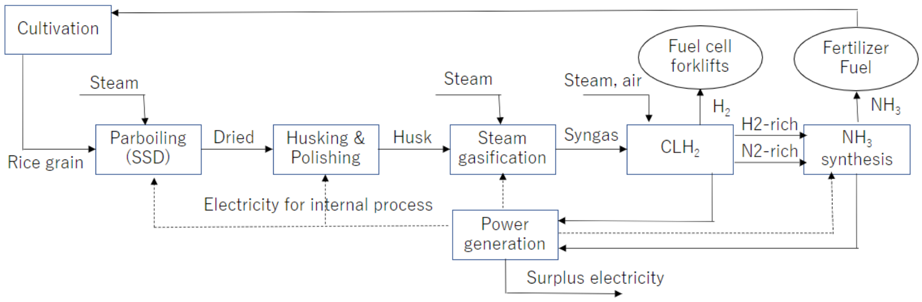

Figure 1: Schematic diagram of the proposed integrated system.

To enhance the energy efficiency throughout the integrated system, enhanced process integration (EPI) is adopted in each module and the whole system. EPI is a technology combining exergy recovery and process integration. EPI has been able to improve the energy efficiency of some systems including NH_3 and power generation from microalgae (Nurdiawati et al., 2019).

2.1. Input parameters

Table 1 shows the ultimate and proximate analyses of rice husk that is used in this study (Darmawan et al., 2018). The average amount of rice grain that could be processed in a rice mill is around 200 t/d.

Table 1: Composition and properties of rice husk used in the study ("db" stands for "dry basis")

Ultimate analysis	Value	Proximate analysis	Value
Hydrogen (wt% db)	4.75	Volatile (wt% db)	63.52
Oxygen (wt% db)	35.47	Fixed carbon (wt% db)	16.22
Nitrogen (wt% db)	0.52	Ash (wt% db)	20.26
Sulfur (wt% db)	0.05	Calorific value (MJ/kg)	18.84
Carbon (wt% db)	38.83		
Chlorine (wt% db)	0.12		
Ash (wt% db)	20.26		

The simulation was conducted using a process simulator of Aspen Plus V11 (Aspen Technology Inc.). Rice husk is defined as a nonconventional solid. PENG-ROB was selected as the base thermodynamic method. The following assumptions were made: (i) the dryer consists of a mixer, a heat exchanger, and a separator; (ii) the atmospheric temperature is 25 °C; (iii) the adiabatic efficiency of the compressor and blower is 90 %; (iv) heat loss is negligible; (v) there is no air contamination inside the dryer; (vi) in the drying process, the heat is completely transferred from the hot material to cold material; (vii) air contains 79 mol% N_2 and 21 mol% O_2.

2.2. Process design of rice grain drying, husking, and polishing

Figure 2 shows the process diagram of the drying process (SSD). The soaked grain is preheated by preheater (HX1) and enters the rotary bed dryer, which is simulated as combination of a mixer (MIX1), a heat exchanger (HX2), and a separator (SEP1). The grain is mixed with steam, acting as a fluidizing agent, in a mixer (MX1) and receives the heat from compressed steam through a heat exchanger (HX2) which is immersed inside the dryer. The steam evaporated during drying and exhausted from the rotary bed is split into two streams: fluidizing steam and compressed steam. The former is used as a fluidizing agent for drying and circulated by using a blower (BL1), while the latter is compressed by using a compressor (COMP1) and used to provide the heat required for drying. In this study, the paddy is dried to a moisture content of 18 % wb for 5 min under drying temperature of 150 °C. The minimum fluidizing steam is 720 kg/h (Taechapairoj et al., 2004). Other assumed conditions are listed in Table 2.

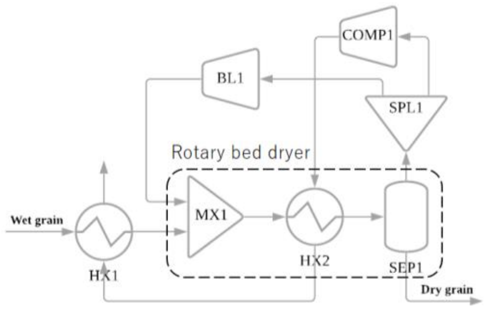

Figure 2: Flow diagram of the drying process including the exergy recovery technology

Table 2: Drying conditions for SSD in this study ("wb" stands for "wet basis")

Properties	Value
Average particle diameter (mm)	3.5
Moisture content before soaking (wt% wb)	26
Moisture content after soaking (wt% wb)	60
Moisture content after SSD (wt% wb)	18
Bed temperature (°C)	150

2.3. Process design of steam gasification and chemical looping H_2 production

In this study, CLH_2 was selected because it can produce H_2 while separating CO_2, with a much simplified process and higher energy efficiency compared to the conventional water gas shift reaction (Fan, 2010). CLH_2 uses metal oxide as an oxygen carrier (OC) to transport oxygen from one reactor to the other. The ideal OC has the following characteristics: high oxygen carrying capacity, recyclability, and mechanical strength to sustain multiple cycles. In this research, Fe-based OC is selected because of its characteristics, such as low cost, high thermal, and mechanical properties (Zaini et al., 2017). However, using only Fe-based OC leads to problem of agglomeration. The utilization of Fe_2O_3/Al_2O_3 is proposed in this study with the consideration of better oxygen transfer capacity, faster reduction rate, better reactivity, and the reduction of sintering. Mass ratio of 70:30 for Fe_2O_3 and Al_2O_3 is used for the simulation because of its high activity and stability for H_2O and CO_2 splitting in chemical looping (Rihko-Struckmann et al., 2016).

Figure 3 represents the process flow diagram of gasification and CLH_2. Both gasification and CLH_2 are operated at an atmospheric pressure. The dried biomass is fed to the gasifier where it is changed to a form of syngas. The produced syngas is fed to the reducer where it reacts with Fe_2O_3 (OC) and forms CO_2 and H_2O. The following reactions are thought to be occurring (Zaini et al., 2017).

$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2 \quad (1)$$

$$FeO + CO \rightarrow Fe + CO_2 \quad (2)$$

$$Fe_2O_3 + H_2 \rightarrow 2FeO + H_2O \quad (3)$$

$$FeO + H_2 \rightarrow Fe + H_2O \quad (4)$$

$$4Fe_2O_3 + 3CH_4 \rightarrow 8Fe + 3CO_2 + 6H_2O \quad (5)$$

The reduced OC enters the oxidizer and is reacted with steam, generating H_2 and Fe_3O_4. The following reactions are assumed to occur in the oxidizer (Zaini et al., 2017).

$$Fe + H_2O \rightarrow FeO + H_2 \quad (6)$$

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2 \quad (7)$$

The OC enters the combustor, where it is mixed with air and forms Fe_2O_3. The following reaction is considered to occur in the combustor (Zaini et al., 2017).

$$4Fe_3O_4 + O_2(air) \rightarrow 6Fe_2O_3(+N_2) \quad (8)$$

The produced heat is carried to the reducer via OC. The exhaust gas from the reducer is used to provide the heat during gasification (HX3) and to generate steam for gasification (HX4). The exhaust gas from the oxidizer is used to generate steam for the oxidizer (HX5), and the remaining heat is used for the steam turbine (ST1). For the steam turbine (ST1), water is pressurized by using a pump (Pump1) and is heated by the exhaust gas from the steam turbine (HX6), the oxidizer (HX7), and the combustor (HX8).

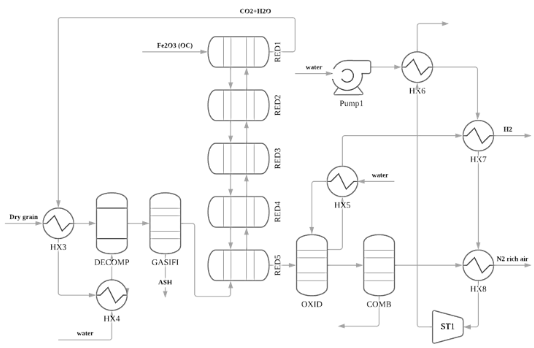

Figure 3: Process flow diagram of gasification, syngas chemical looping (CLH_2).

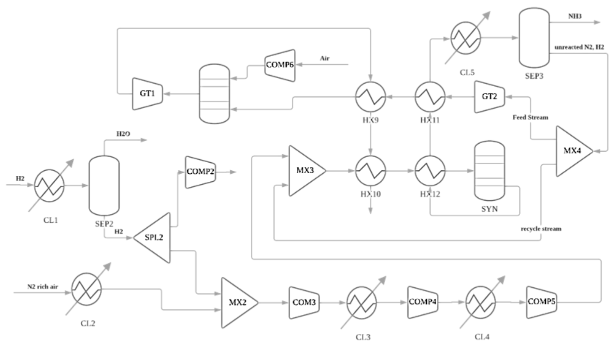

Figure 4: Process flow diagram of NH_3 synthesis module.

2.4. Process design of NH_3 synthesis

Figure 4 shows the NH_3 synthesis module. H_2-rich gas from the oxidizer and N_2-rich gas from the combustor are cooled to 25 °C (CL1,2) and H_2O is separated (SEP2). The two streams are mixed together and are compressed to 15 MPa (COMP3,4,5). Reese et al. (2016) have tested that a small scale Haber process could run with a feed of 40 mol-N_2/h and 140 mol-H_2/h. The optimal molar ratio of H_2 and N_2 for NH_3 production is 3 to 1 (Nurdiawati et al., 2019). H_2 burns when it is mixed with O_2 at a H_2/O_2 ratio of 4.5~94.0 vol%; hence, it is essential to avoid this range. The compressed stream is preheated by the exhaust gas from the gas turbine and the NH_3 synthesis module (HX10,12) and is sent to the NH_3 synthesis module. For the NH_3 synthesis, Fe-promoted catalyst is used and the reaction is operated at 450 °C. During synthesis, the following reaction occurs.

Table 3: Parameters for CLH_2 and NH_3 production

Properties	Value	Properties	Value
Gasification condition	700 °C, 0.1013 MPa	Turbine efficiency	90 %
Steam-to-biomass ratio (S/B)	0.7	Max gas turbine inlet temp.	1,500 °C
Oxygen carrier	Fe_2O_3 (0.7 Fe_2O_3, 0.3 Al_2O_3)	Max steam turbine inlet temp.	600 °C
Reducer temp. and pressure	800-950 °C, 0.1013 MPa	Steam pressure	10 MPa
Oxidizer temp. and pressure	750-900 °C, 0.1013 MPa	Compressor efficiency	90 %
Combustor temp. and pressure	1,300 °C, 0.1013 MPa	Pump efficiency	75 %
Synthesis temp. and pressure	450 °C, 15 MPa	Minimum temp. approach	20 °C
Catalyst for N_3 synthesis	Iron	H_2/N_2 ratio	3
Recycle to feed streams molar ratio	1.5-3.5		

The conversion efficiency for the synthesis reaction is around 20–30 %. The unreacted gas has to be recycled so the produced gas is cooled to 25 °C (CL5) to separate NH_3 with unreacted H_2 and N_2. A part of the unreacted gas must also leave the loop in order to avoid accumulation of substances, such as Ar, so the unreacted gas is split into two streams, the feed-stream and the recycled-stream. The recycled-stream is sent back to the NH_3

synthesis module. The feed-stream is decompressed to 3 MPa (GT2), an optimal pressure for running the gas turbine, and is combusted (COMB2) with air to generate electricity in the gas turbine (GT1). Table 3 shows the rest of the parameters for CLH_2 and NH_3 synthesis.

2.5. Performance evaluation

Two energy efficiencies are used in this study to evaluate the performance: NH_3 production efficiency (η_{NH3}), power generation efficiency (η_{power}). They are calculated according to the following equations based on the lower heating value (LHV).

$$\eta_{power} = \frac{W_{net}}{m_{dried\ paddy} \cdot LHV_{dried\ paddy}} \tag{9}$$

$$\eta_{NH3} = \frac{m_{NH3} \cdot LHV_{NH3}}{m_{dried\ paddy} \cdot LHV_{dried\ paddy}} \tag{10}$$

$$W_{net} = \sum W_{GT} + \sum W_{ST} + \sum W_{EX} - \sum W_{CP} - \sum W_P \tag{11}$$

where, W_{net} represents the net power generated from the system (MW). m_{NH3} and $m_{dried\ paddy}$ are the mass flow of NH_3 and the paddy in kg/s, respectively. $LHV_{dried\ paddy}$ and LHV_{NH3} represent the LHVs of the paddy and NH_3 in MJ/kg, respectively. W_{GT}, W_{ST}, W_{EX}, W_{CP} and W_P represent the generated power or duty of the gas turbine (GT1,2), steam turbine (ST1), heat exchangers (HX1-12), compressor (COMP1-6, BL1), and pump (Pump1) in MW, correspondingly.

3. Results and discussion

3.1. Effect of CLH_2 temperature

Figure 5a illustrates the effect of reduction temperature to the generated power and energy efficiencies. The temperature of the oxidizer was set to 50 °C lower than that of the reducer. As the temperature increases, the power efficiency increases, and the NH_3 efficiency decreases after 900 °C. The power efficiency increases because the exhaust gas from the oxidizer heats the steam that rotates the steam turbine even more. The NH_3 efficiency decreases after 900 °C because the H_2 yield decreases, as shown in Figure 6b. This is due to the reduction of the amount of OCs circulated in the CLH_2 module.

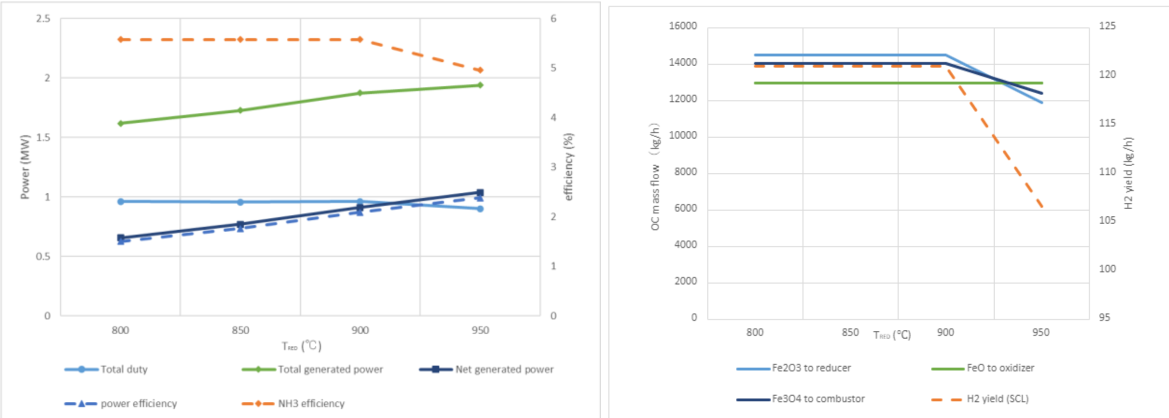

Figure 5: (a) Power, duty and efficiency of the system at different reduction temperatures. (b) efficiency at different S/B ratios (S/B ratio = 0.7 and recycle ratio = 3)

3.2. Effect of recycle to feed stream ratio for NH_3 synthesis

The amount of H_2 produced is around 60 kmol/h and the amount of N_2 produced is around 120 kmol/h, so they are sufficient to run as a small-scale Haber-Bosch process. The volume ratio of the amount of H_2 and O_2 entering the NH_3 synthesis process is around 99.5 %, so there is no risk of H_2 combustion. Figure 6a illustrates the effect of recycled-to-feed stream ratio to the generated power and efficiencies. As the recycled-to-feed stream ratio is increased from 1.5 to 3.5, the NH_3 production increases by 22.4 %. In simulation, the largest amount of NH_3 produced is 487 kg/h per 8,333 kg/h of rice husk. As the recycled-to-feed stream ratio is increased from 1.5 to 3.5, the net generated power decreases by 10.4 %. This is due to the decrease of H_2 gas in the combustion reactor for gas turbine. The highest NH_3 and power generation efficiencies are 5.77 % and 1.96 %, respectively. This result is relatively low compared to previous research because it still focuses only on building the outline of the system and increasing the efficiency has yet to be researched. The previous research conducted the CLH_2 at 3 MPa, which helped the net generated power to increase.

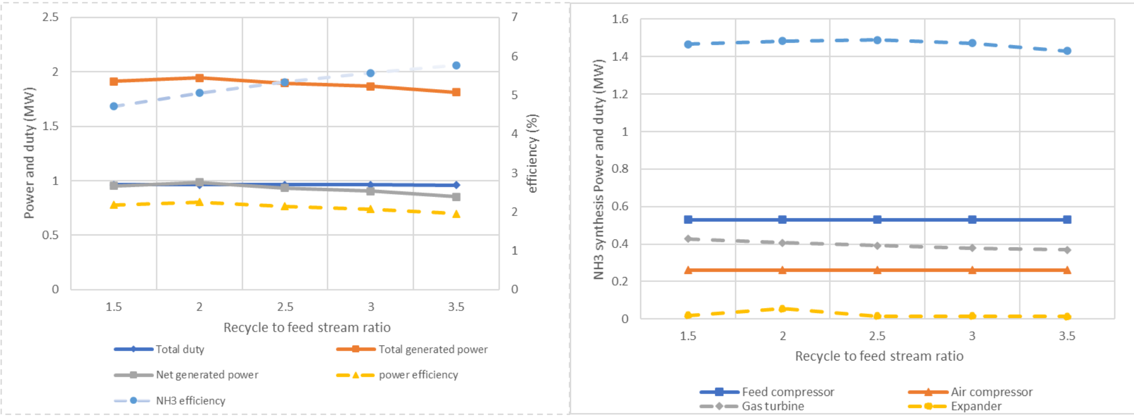

Figure 6: (a)generated power and efficiencies at different recycle ratios (S/B ratio = 0.7 and T_{RED} = 900 °C). (b) Power and duty of each unit at different stream ratios (S/B ratio = 0.7 and T_{RED} = 900 °C).

4. Conclusion

The proposed system shows power energy efficiency of up to 1.96 % and NH_3 production efficiency of up to 5.77 %, under conditions of the S/B ratio of 0.7, reduction temperature of 900 °C, and recycled-to-feed stream ratio of 3.5. This result suggests that NH_3 production from rice husks is a technically and environmentally acceptable approach. However, to gain an efficiency as high as previous research, simulation using higher pressure CLH_2 and further work on process optimization are needed. In addition, a techno-economic assessment is necessary before implementing this system in the real world.

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