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Article in Chemical Engineering Transactions · December 2021

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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 (CLH₂) is a new technology used to produce H₂ from fuel while separating CO₂ 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 H₂ 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. Fe₂O₃ and Al₂O₃ are used as oxygen carrier and heat carrier for CLH₂. The energy efficiency is evaluated using Aspen Plus. The effect of chemical looping temperature, and the effect of recycle to feed stream ratio for NH₃ synthesis were selected for the parameters and evaluated. The highest NH₃ efficiency achieved through the simulation was 5.77 % and the power efficiency was 1.96 %.

1. Introduction

Hydrogen (H₂) 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 H₂, 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 H₂ 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 H₂, which is also an important aspect for broader utilization.

The conventional H₂ 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 H₂ production (CLH₂) technology is receiving intensive attention due to its free-carbon characteristics and high conversion efficiency (Fernández and Abanades, 2016).

Although H₂ has advantageous characteristics, its volumetric energy density is very low (only about 3 Wh/L). Hence, more efficient H₂ storage, both gravimetric and volumetric H₂ densities, is urgently demanded. Among many H₂ storage technologies, NH₃ is a preferred option because of its high storage capacity, applicability, economic performance, and H₂ density. Haber-Bosch process, the main process for NH₃ production, utilizes purified N₂ and H₂ and reacts them under high temperature (400–550 °C) and high pressure (up to 30 MPa) condition, which is highly energy consuming. Nurdawati et al. (2019) proposed an integrated system of CLH₂ and NH₃ synthesis by utilizing the H₂-rich gas from the oxidizer and N₂-rich gas from the combustor and achieved a high total energy efficiency of up to 64.3 % and showed high affinity between CLH₂ and NH₃ synthesis. However, this research focused on microalgae, not the rice industry.

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 NH_3 can be utilized whether as agricultural fertilizer or fuel. The integrated system is considered able to realize a new circular economy in agricultural sector.

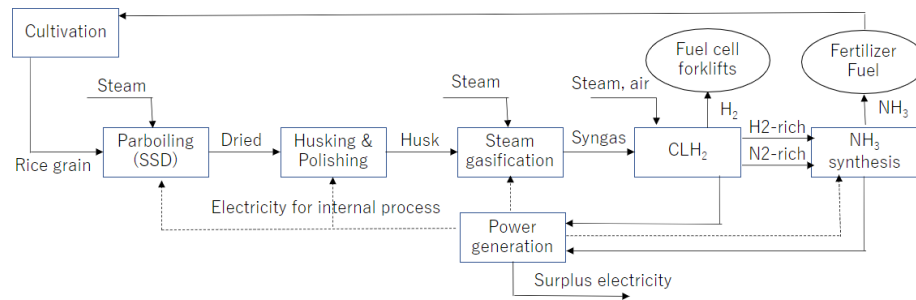


Figure 1: Schematic diagram of the proposed integrated system.

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 (MX1), 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.

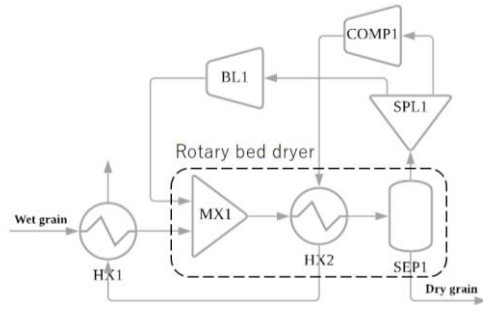


Table 2: Drying conditions for SSD in this study (“wb” stands for “wet basis”)

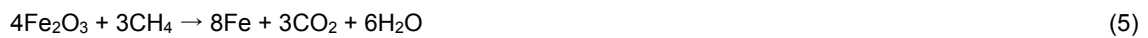
Properties	Value
Average particle diameter (mm)	3.5
Moisture content before soaking (wt% wb)	26
Moisture content after soaking (wt% wb)	60
Moisture content after SSD (wt% wb)	18
Bed temperature (°C)	150

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

2.3. Process design of steam gasification and chemical looping H₂ production

In this study, CLH₂ was selected because it can produce H₂ while separating CO₂, with a much simplified process and higher energy efficiency compared to the conventional water gas shift reaction (Fan, 2010). CLH₂ 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 Fe₂O₃/Al₂O₃ 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 Fe₂O₃ and Al₂O₃ is used for the simulation because of its high activity and stability for H₂O and CO₂ splitting in chemical looping (Rihko-Struckmann et al., 2016).

Figure 3 represents the process flow diagram of gasification and CLH₂. Both gasification and CLH₂ 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 Fe₂O₃ (OC) and forms CO₂ and H₂O. The following reactions are thought to be occurring (Zaini et al., 2017).



The reduced OC enters the oxidizer and is reacted with steam, generating H₂ and Fe₃O₄. The following reactions are assumed to occur in the oxidizer (Zaini et al., 2017).



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).



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).

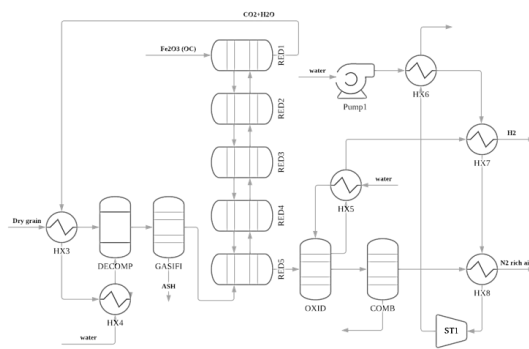


Figure 3: Process flow diagram of gasification, syngas chemical looping (CLH₂).

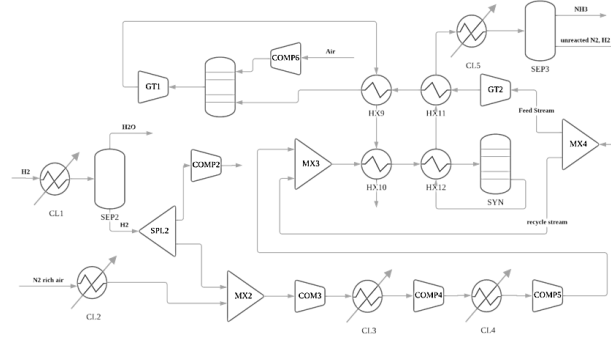


Figure 4: Process flow diagram of NH₃ synthesis module.

2.4. Process design of NH₃ synthesis

Figure 4 shows the NH₃ synthesis module. H₂-rich gas from the oxidizer and N₂-rich gas from the combustor are cooled to 25 °C (CL1,2) and H₂O 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-N₂/h and 140 mol-H₂/h. The optimal molar ratio of H₂ and N₂ for NH₃ production is 3 to 1 (Nurdiawati et al., 2019). H₂ burns when it is mixed with O₂ at a H₂/O₂ 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 NH₃ synthesis module (HX10,12) and is sent to the NH₃ synthesis module. For the NH₃ synthesis, Fe-promoted catalyst is used and the reaction is operated at 450 °C. During synthesis, the following reaction occurs.

Table 3: Parameters for CLH₂ and NH₃ 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 ₂ O ₃ (0.7 Fe ₂ O ₃ , 0.3 Al ₂ O 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 NH₃ with unreacted H₂ and N₂. 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 NH₃

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 CLH₂ and NH₃ synthesis.

2.5. Performance evaluation

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

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

$$\eta_{NH_3} = \frac{m_{NH_3} \cdot LHV_{NH_3}}{m_{dried\ paddy} \cdot LHV_{dried\ paddy}} \quad (10)$$

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

where, W_{net} represents the net power generated from the system (MW). m_{NH_3} and $m_{dried\ paddy}$ are the mass flow of NH₃ and the paddy in kg/s, respectively. $LHV_{dried\ paddy}$ and LHV_{NH_3} represent the LHVs of the paddy and NH₃ 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 CLH₂ 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 NH₃ 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 NH₃ efficiency decreases after 900 °C because the H₂ yield decreases, as shown in Figure 6b. This is due to the reduction of the amount of OCs circulated in the CLH₂ module.

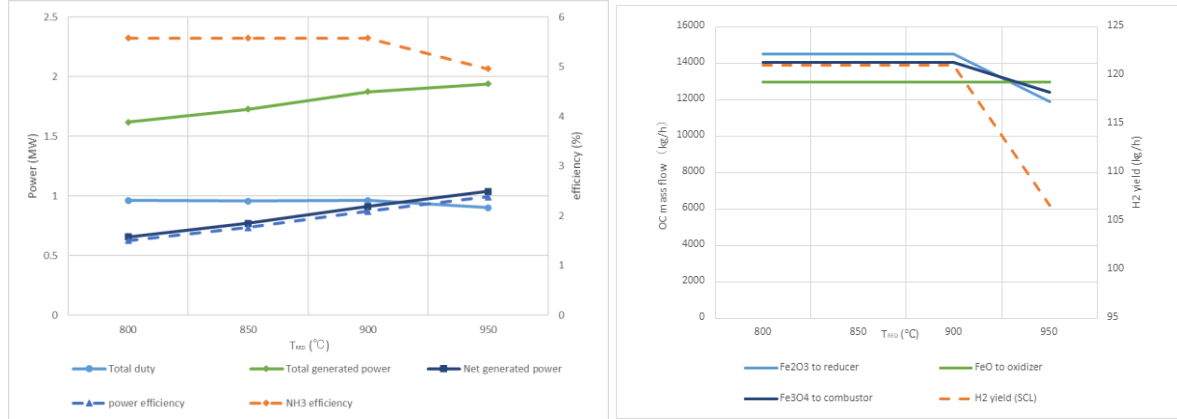


Figure 5: (a) Power, duty and efficiency of the system at different reduction temperatures. (b) efficiency at different S/B ratios (S/B ratio = 0.7 and recycle ratio = 3)

3.2. Effect of recycle to feed stream ratio for NH₃ synthesis

The amount of H₂ produced is around 60 kmol/h and the amount of N₂ 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 H₂ and O₂ entering the NH₃ synthesis process is around 99.5 %, so there is no risk of H₂ 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 NH₃ production increases by 22.4 %. In simulation, the largest amount of NH₃ 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 H₂ 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.

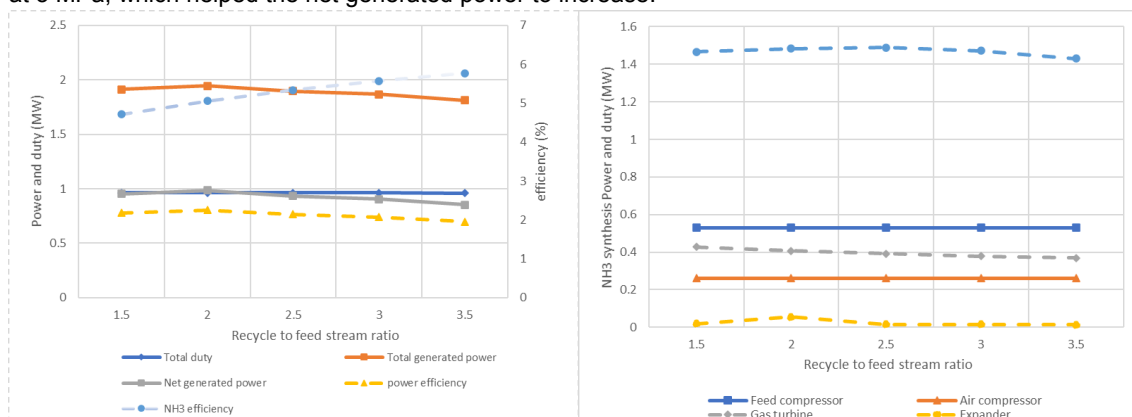


Figure 6: (a) generated power and efficiencies at different recycle ratios (S/B ratio = 0.7 and $T_{RED} = 900\text{ }^{\circ}\text{C}$). (b) Power and duty of each unit at different stream ratios (S/B ratio = 0.7 and $T_{RED} = 900\text{ }^{\circ}\text{C}$).

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 $900\text{ }^{\circ}\text{C}$, 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.

Acknowledgements

The research is funded by JSPS KAKENHI Grant Number JP19K04211.

References

- Darmawan A., Fitrianto A.C., Aziz M., and Tokimatsu K., 2018, Integrated System of Rice Production and Electricity Generation, *Applied Energy*, 220, 672–680.
- Fan L.S., 2010, Chemical Looping Gasification Using Gaseous Fuels, Chapter In: *Chemical Looping Systems for Fossil Energy Conversions*, American Institute of Chemical Engineers/John Wiley & Sons, USA, 215–300.
- Fernández J., Abanades J., 2016, Novel Process for Hydrogen Production Through the Sorption Enhanced Reforming of Methane Combined with Chemical Looping Combustion, *Chemical Engineering Transactions*, 52, 535–540.
- Lay C.H., Hsu Y.C., Lin C.Y., and Chen C.C., 2020, Anaerobic Biohydrogen Production Using Rice Husk-Based Biologics, *Waste and Biomass Valorization*, 11, 1059–1068.
- Nurdiawati A., Zaini I.N., Amin M., Sasongko D., and Aziz M., 2019, Microalgae-Based Coproduction of Ammonia and Power Employing Chemical Looping Process, *Chemical Engineering Research and Design*, 146, 311–323.
- Reese M., Marquart C., Malmali M., Wagner K., Buchanan E., McCormick A., and Cussler E.L., 2016, Performance of a Small-Scale Haber Process, *Industrial and Engineering Chemistry Research*, 55, 3742–3750.
- Rihko-Struckmann L.K., Datta P., Wenzel M., Sundmacher K., Dharanipragada N.V.R.A., Poelman H., Galvita V.V., and Marin G.B., 2016, Hydrogen and Carbon Monoxide Production by Chemical Looping over Iron-Aluminium Oxides, *Energy Technology*, 4, 304–313.
- Taechapairoj C., Prachayawarakorn S., and Soponronnarit S., 2004, Characteristics of Rice Dried in Superheated-Steam Fluidized-Bed, *Drying Technology*, 22, 719–743.
- Zaini N.I., Nurdiawati A., and Aziz M., 2017, Cogeneration of Power and H_2 by Steam Gasification and Syngas Chemical Looping of Macroalgae, *Applied Energy*, 207, 134–145.