Separated Biochar and Pyrolysis Gas of Biomass via Chemical Looping for Methanol and Ammonia Production

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In this research, a novel integrated methanol and ammonia production via chemical looping is developed utilizing the separated biochar and pyrolysis gas from fast pyrolysis unit. The proposed system uses biomass as a feedstock due to its huge global potential. Process modelling and evaluation are conducted using a steady-state process simulator. The fixed bed pyrolysis is adopted to separate pyrolysis gas and biochar. The pyrolysis gas is processed in the steam bio-oil reformer for hydrogen production, while the biochar is fed to the chemical looping unit as a reducing agent. Other processes, including hydrogen separation and thermal energy circulation processes for hydrogen production, are proposed and simulated based on the previous studies. The by-produced CO_2 from the reducer of the chemical looping unit is processed with H_2 produced from a steam bio-oil reformer to produce methanol. In addition, to increase the overall efficiency, ammonia is synthesized using hydrogen and nitrogen produced from the oxidizer and combustor of the chemical looping unit. This novel system is expected to be able to produce both methanol and ammonia from low-rank feedstock with high energy efficiency. The highest methanol and ammonia production efficiency achieved through the simulation was 10.3 % and 29.2 %.

1. Introduction

Methanol is one of the promising fuels due to its simple transport and storage and has a high bulk density with a large demand market and prospect (Huang et al., 2022). There are some pathways for producing methanol via conversion of fossil fuels (like natural gas and coal) and renewable sources (such as biomass, biogas, and carbon dioxide). Large-scale methanol production tends to be dominated by steam methane reforming (Adnan and Kibria, 2020) or coal gasification (Zhang et al., 2020), which depends on the suitable location for the plant. The methanol production line includes the following process: syngas production, syngas purification, and methanol synthesis. For the first step, natural gas or coal is gasified, producing a mixture of CO, CO_2, and H_2. Oxygen from the air separation unit (ASU) is fed into the combustion reactor along with combustible gas to provide heat for the steam methane reforming (SMR) reaction and gasification reaction. Then the produced syngas is put into the water gas shift (WGS) reaction to increasing the amount of H_2 and mixed with the unconverted syngas. Finally, methanol synthesis takes over to produce crude methanol. Crude methanol is usually separated by gas-liquid separation. Traditional methanol production, as previously mentioned, is an unsustainable process and also requires high energy because it still uses fossil fuels as feedstock and consumes high electrical energy for air separation and CO_2 capture (Garcia et al., 2021).

On the other hand, ammonia production still uses natural gas as its feedstock. In the ammonia production process, natural gas and air are needed to provide hydrogen and nitrogen needs. On an industrial scale, the ammonia synthesis process can use SMR, WGS, methanation, and the Haber-Bosch (H-B) process (Zhang et al., 2020). In these processes, the main problem faced is that the produced CO_2 requires chemical absorption (such as monoethanolamide) or physical absorption (such as Pressure Swing Absorption (PSA)), which is very energy-consuming and expensive. In addition, regulating the flow of steam and air to ensure the ratio of the molar ratio of $H_2:N_2$ at 3:1 condition is difficult because the composition of natural gas is not always the same. Biomass, as a promising renewable source, can replace coal and natural gas to achieve sustainability and reduce negative impacts on the environment. In addition, biomass can be converted into H_2, CO_2, and N_2

through pyrolysis, gasification, steam reforming, and chemical looping processes (Parthasarathy and Narayanan, 2014). In producing pure H_2, N_2, and CO_2, needed in the production process of methanol and ammonia, the conversion process must be integrated. The study about separated pyrolysis to produce H_2 was studied by Situmorang et al. (2020). To produce both ammonia and methanol from biomass feedstock could enhance the efficient and effective integrated processing plant. If the production of both of them can be implemented, the negative carbon will be achieved from biomass conversion process to another fuel. However, there is almost no advanced study to convert the biomass to methanol and ammonia simultaneously. In this study, a novel integration of separated pyrolysis, steam reforming, chemical looping, H-B, and methanol synthesis process is proposed. This research goal is to achieve high energy efficiency through process integration.

2. Proposed integrated system

The proposed system consists of five processes, including separated pyrolysis, steam reforming of pyrolysis gas, biochar chemical looping, ammonia synthesis via H-B, and methanol synthesis via hydrogenation. Figure 1 shows the schematic flow diagram of the materials and energy in the integrated system. The proposed system uses gamal tree (*Gliricidia sepium*) as feedstock which has a high calorific value. The feedstock entering the pyrolysis module is converted to pyrolysis gas and biochar. The separated pyrolysis gas then goes to steam reforming to produce H_2 and separated tar product. On the other hand, biochar enters the chemical looping module to produce H_2, CO_2, and N_2 via reduction-oxidation process using metal oxide in the reducer, oxidized, and combustor.
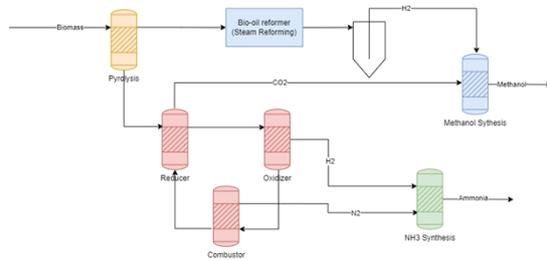
Figure 1: Schematic diagram of the proposed integrated system

Table 1: Composition and properties of gamal tree used in study (dry base,db)

Ultimate Analysis	Value	Proximate Analysis	Value
Hydrogen (wt% db)	5.69	Volatile (wt% db)	75.60
Oxygen (wt% db)	42.15	Fixed carbon (wt% db)	20.12
Nitrogen (wt% db)	0.94	Ash (wt% db)	4.28
Sulphur (wt% db)	0.05	Calorific value (kcal/kg)	4,472
Carbon (wt% db)	46.87		
Chlorine (wt% db)	0.12		
Ash (wt% db)	4.28		

Table 2: Input parameters and main process simulation assumptions

Item	Parameters and description
Biomass mass flow	Gamal tree, m = 1 kg/s
Pyrolysis	RYield and RStoic, Sep. 500 °C, 1 bar
	All N and S components carried out in biochar stream
Gasifier	RYield, Decomposition: P = 3 MPa, T = 400 °C
	RGibbs, Reduction: P = 3 MPa, T = 1,300 °C
	Medium: Steam = 0.04 kg/s
Steam Reforming	RGibbs, T= 850 °C, P = 1 bar, catalyst: Nickel
PSA	Separator Block, T = 35 °C, P = 7 bar
Biochar Chemical Looping	Reducer: P = 3 MPa, T = 900 °C; Oxidizer: P = 3 MPa, T = 700 °C; Combustor: P = 3.1 MPa; Oxygen Carrier: Fe_2O_3:Al_2O_3, m = 1-15 kg/s; CO_2 recycling ratio: 0.1-0.8; Steam = 3 kg/s; Air: 79 % N_2, 21 % O_2, m = 1 kg/s
Boiler	RGibbs, 10 bar
Methanol Synthesis	RGibbs, T = 220 °C, P = 35 bar
Distillation Column	Module: RadFrac; 20 th and 10 th stages for crude methanol intake; Reflux: 2; Tcon = 30 °C; For Configuration 1: Treb = 101.4 °C; Distillate to feed ratio: 0.85; Qcon = -2,026 kW, Qreb = 2,047 kW; For Configuration 2: Treb = 99.8 °C; Distillate to feed ratio: 0.5; Qcon = -1,788 kW, Qreb = 1,857 kW.
Ammonia Synthesis	RStoic, T = 450 °C, P = 15 MPa, catalyst: Iron
Heat Exchanger	Minimum temperature different approach ΔT_{min} = 20 °C; HX2, ΔT_{min} = 50 °C
Expander/Compressor/Pump	Mechanical efficiency: 90 %

2.1 Input parameters

Table 1 shows the ultimate and proximate analysis of gamal tree used in this study. The simulation is conducted using Aspen Plus V12 (Aspen Technology Inc) for process modelling. Gamal tree is defined as a non-conventional solid. Peng-Robinson-Boston-Matias (PR-BM) is selected as the global thermodynamic model. PR-BM is suitable for all temperature and pressure range simulations. The following assumptions are made: (i) there is no moisture in feedstock; (ii) the atmospheric temperature is 25 °C; (iii) the adiabatic efficiency of the compressor and pump is 90 %; (iv) heat loss is negligible; (v) air contains 79 mol% N_2 and 21 mol% O_2.

2.2 Process design of separated pyrolysis

Pyrolysis is a thermochemical process that aims to decompose biomass in the absence of oxygen at a temperature range from 350 to 700 °C, where biochar, pyrolysis gases, and non-condensable gases, such as CO, CO_2, CH_4, and H_2, are produced together from biomass. The pyrolysis of biomass can be divided into two different processes, namely slow and fast pyrolysis, based on the heating rate. Slow pyrolysis always produces more biochar from biomass, while fast pyrolysis will produce more pyrolysis gas.

The biomass pyrolysis process is simulated by integrating RYield reactor for biomass drying (DRYING) and decomposition (PYRO) and a series of separators (SEP-1 and SEP-2) to separate the volatiles and biochar parts. RStoic (DECOMP) is used to generate gases from a partial proportion of the volatiles. The volatiles and biochar parts are presented as the composition of C, H, N, S, O, and H_2O, while the produced gases are assumed to be CO, CO_2, CH_4, and H_2.

2.3 Process design of biochar chemical looping and ammonia synthesis

In this simulation, CLH is selected for processing the biochar to become H_2 while separating CO_2 via efficient energy consumption compared to the conventional process. For this process, the metal oxide is used as an oxygen carrier (OC) to transport the oxygen between three reactors (reducer, oxidizer, and combustor). In this study, Fe-based OC is selected due to its characteristics, such as low cost and high thermal and mechanical properties. To avoid 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.
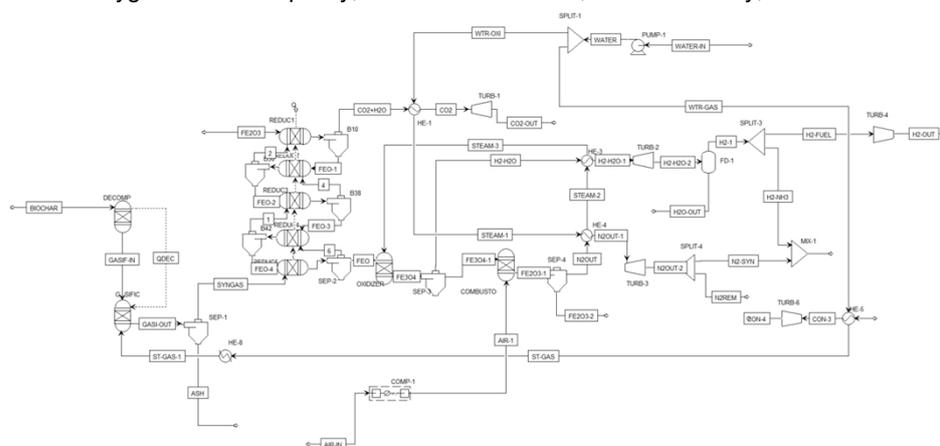
Figure 2: Process flow diagram of syngas chemical looping of biochar

Figure 2 shows the process flow diagram of gasification and CLH. Both systems work at atmospheric pressure. The biochar is fed to the gasifier where it is converted to syngas. The produced syngas is fed to the reducer where it reacts with Fe_2O_3 and forms CO_2 and H_2O. The reduced OC enters the oxidizer and is reacted with steam, generating H_2 and Fe_3O_4. The OC enters the combustor, where it is mixed with air and forms Fe_2O_3 and N_2.

Figure 3 represents the ammonia synthesis module. H_2 gas from the oxidizer and N_2 gas from the combustor reactor are cooled to 25 °C while H_2O is separated. The two streams are mixed and are compressed to 15 MPa. The optimal molar ratio of H_2 and N_2 for ammonia production is 3 to 1 (Nurdiawati et al., 2019). Thereafter, H_2 burns when mixed with O_2 at H_2/O_2 ratio of 4.5. The compressed stream is preheated by the exhaust gas from the gas turbine and the ammonia synthesis module and is sent to the ammonia synthesis module. For enhancing ammonia synthesis, the Fe catalyst is added, and the reaction is operated at 450 °C.

Figure 3: Process flow diagram of ammonia synthesis module

2.4 Process design of steam reforming and methanol synthesis

Figure 4 introduces the steam reforming of pyrolysis gas. Steam reforming of pyrolysis gas and bio-oil is also considered the most effective and promising route to convert it to H_2 or syngas for clean applications. It can be explained that the CO produced in this process can react with excess steam through a water-gas shift reaction to produce higher H_2. A commercial Ni-based catalyst having a good activity for vapor reforming of bio-oil is employed, and the deactivated catalyst can also be easily reused if needed.

Figure 5 shows the methanol synthesis module. This module consists of a methanol synthesis reactor, gas separator, and purifier. CO_2 from the reducer and H_2 from steam reforming are then mixed and fed to the methanol synthesis reactor. The detailed conditions are: (a) the methanol is produced at 79 % selectivity, 20 % yield, and 25 % CO_2 conversion; (b) operating pressure and temperature are set to 7 MPa and 250 °C, and (c) the ratio of H_2-to-CO_2 is 3. To achieve high purity of methanol, methanol and H_2O, which are generated from synthesis, are separated using a column.

Figure 4: Process flow diagram of steam reforming of pyrolysis gas

Figure 5: Process flow diagram of methanol synthesis module

2.5 Performance evaluation

In this study, two energy efficiencies are used for evaluating the system performance: Methanol production efficiency ($\eta_{CH_3OH\ production}$) and ammonia production efficiency ($\eta_{NH_3\ production}$).

$$\eta_{CH_3OH\ production} = \frac{m_{CH_3OH}.LHV_{CH_3OH}}{m_{biomass}.LHV_{biomass}} \tag{1}$$

$$\eta_{NH_3\ production} = \frac{m_{NH_3}.LHV_{NH_3}}{m_{biomass}.LHV_{biomass}} \#(2)$$

where, m_{NH_3}, m_{CH_3OH}, and $m_{biomass}$ are the mass flow of ammonia, methanol, and the gamal tree in kg/s. $LHV_{biomass}$, LHV_{CH_3OH}, and LHV_{NH_3} represent the lower heating values of gamal tree, methanol, and ammonia in MJ/kg.

3. Result and discussion

3.1 Effect of S/C (steam-to-carbon) ratio

The increase in S/C ratio will increase the conversion and reduce the carbon formation. For the bio-oil and pyrolysis gas reforming, it is obtained that the S/C ratio of around 5.0 correlated to high conversion as a high CO/H_2 ratio in the produced gas. Figure 6 shows the effect of S/C ratio on the total ammonia production and net power in the system. H_2 production increases in proportion to the increasing S/C ratio like the research which conducted by Situmorang et. al. (Situmorang et al., 2020), which influences the increase of ammonia production because H_2 has a high portion compared to N_2 for ammonia synthesis reaction. Increasing S/C ratio affects the energy demand for an endothermic reaction, which decreases the flue gas temperature, leaving from the thermal insulation of the ammonia synthesis reformer. Appropriately, the S/C ratio of 5 is chosen as the optimum condition for this process.
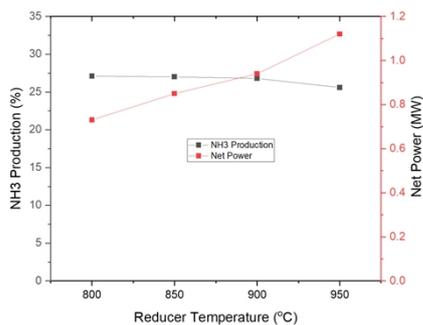
Figure 6: Methanol production efficiency and net power at different S/C ratio
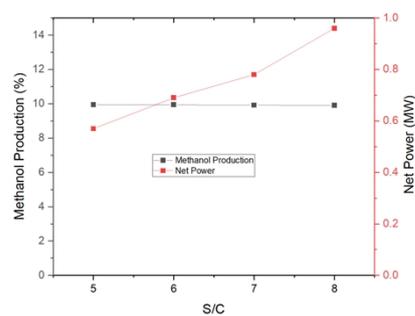
Figure 7: Ammonia production efficiency and net power at increasing reducer temperature

3.2 Effect of recycle to feed stream ratio for ammonia synthesis and methanol synthesis
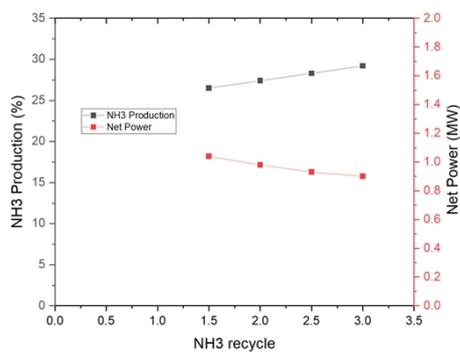
Figure 8: Methanol production efficiency and net power at different methanol recycle ratio
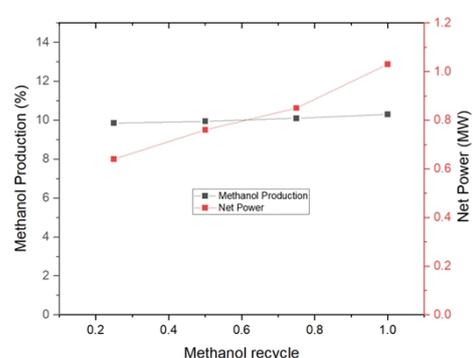
Figure 9: Ammonia production efficiency and net power at different ammonia recycle ratio

The amount of H_2 produced is around 70 kmol/h and N_2 produced is around 150 kmol/h. Therefore, H_2 and N_2 are adequate to be reacted in a small-scale H-B process. For the volume ratio, the amount of H_2 and O_2 entering the ammonia synthesis process is around 99.5 %, which translates to no risk of H_2 combustion occurrence. Figure 9 shows the effect of recycled-to-feed stream ratio on the generated power and efficiency of ammonia production. From the figure above, if recycled-to-feed stream ratio is increased from 1.5 to 3.0, the ammonia production increases by 10.2 %. From the simulation result, the highest efficiency is 29.2 % obtained in ammonia recycled-to-feed stream ratio of 3. Similarly, produced methanol also increases in case the recycled-to-feed stream ratio is increased from 0.25 to 1.0, as shown in Figure 8. The highest ratio (1.0) leads to the highest efficiency of 10.3 %. The net power decreases because of the decrease of H_2 gas in the combustion of gas turbines in ammonia and methanol modules which also founded from the research of Hakandai et. al (2022).

3.3 Effect of reducer temperature

Figure 7 shows the effect of reduction temperature on the generated power and energy efficiencies. As the temperature increases, the power efficiency increases, and the ammonia 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 ammonia efficiency decreases after 900 °C because the H_2 yield decreases. This is due to the reduction of the number of OCs circulated in the CLH module. This condition affects the ammonia production because the H_2 fed decreases so that the minimum ratio of H_2 and N_2 is not appropriate which like Miyahira and Aziz (2021) studied.

4. Conclusion

The proposed integrated system presents high ammonia production efficiency of up to 29.2 %, under conditions of the S/C ratio of 5.0, reduction temperature of 800 °C, and recycled-to-feed stream ratio of 3.0. On the other hand, the methanol production can have an efficiency of up to 10.3 % under conditions of the S/C ratio of 5.0, reduction temperature of 800 °C, and recycled-to-feed stream ratio of 1.0. This result suggests that simultaneous ammonia and methanol production from biomass via separated pyrolysis integrated with steam reforming and chemical looping is technically and environmentally acceptable. However, to get efficiency as high as previous research, simulation using higher pressure CLH and optimization of catalyst in steam reforming are necessary to be performed.

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