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Production of Ammonia from Low Rank Coal Employing Chemical Looping and Haber-Bosch Process

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An integrated production system of ammonia from low rank coal (LRC) is proposed and evaluated in this study. It unites several processes: coal direct chemical looping, nitrogen production, ammonia synthesis, and power generation. To effectively integrate and minimize the formation of exergy destruction throughout the integrated system, the concepts of exergy recovery and process integration are adopted. LRC is initially dried to low moisture content and ground. In coal direct chemical looping, three circulated reactors are adopted: reducer, oxidizer and combustor. The pulverized LRC is directly reacted with the oxygen carrier in the reducer producing CO_2. In addition, the reduced oxygen carrier is then reacted with steam in oxidizer to produce H_2. Finally, the oxygen carrier is finally oxidized using O_2-rich gas in combustor to return to its initial state. The produced H_2 is then reacted with N_2, which is produced in N_2 separation unit, in NH_3 synthesis. The generated heat throughout the integrated system, especially chemical looping and NH_3 synthesis, is recovered for power generation. Some operating parameters, including target moisture content in drying, pressure during chemical looping, and carbon conversion efficiency during reduction, are evaluated in terms of total energy efficiency. The proposed integrated-system shows relatively high energy efficiency, which is about 75 %.

1. Introduction

Ammonia (NH_3) is one of the largest produced chemicals in the world after sulphuric acid. Currently, it is largely utilized in agriculture as fertilizer (about 80%) while the rest is broadly used as secondary material for production of pharmaceutical, refrigeration, explosives and cleaning material (Giddey et al., 2013). At present, NH_3 is converted mainly from natural gas, coal and oil. However, NH_3 production consumes very huge energy input and cover about 2 % of the total primary energy consumption (Tanabe and Nishibayashi, 2013). Advanced NH_3 synthesis having high energy efficiency is urgently demanded.

NH_3 is potential to store the H_2 in terms of H_2 content (17.6 wt%) and stability. In addition, it has higher H_2 energy density compared to liquefied H_2. In energy utilization, NH_3 can be utilized as fuel for internal combustion engine, fuel cell, and combustion for turbine. NH_3 can be stored in liquid condition under relatively low pressure (0.9 - 1 MPa) under ambient temperature. It leads to the possibility to store NH_3 using the available low pressure tanks, similar to those used for LNG.

On the other hand, as primary energy source, coal has very large reserve leading to its dominant utilization in the future. However, as the environmental awareness increases in the last decade, the decarbonisation of coal has received intensive attention and been accelerated. Among the available large reserve of coal, low rank coal (LRC), including sub-bituminous coal and lignite, has a share of more than its half (Aziz et al., 2016a). However, LRC utilization as energy source still lags behind compared to other resources due to its unfavourable characteristics including high moisture content, less carbon content, and low calorific value (Aziz et al., 2015). Decarbonisation of LRC to H_2 and further storage to NH_3 is considered as potential breakthrough to realize highly-efficient LRC utilization. An in-situ integrated system can give the solution to the problems related to energy density, storage, transportation, and environment.

Based on the above background, NH_3 production system from LRC with high total energy efficiency but low CO_2 emission is demanded. Unfortunately, to the best author's knowledge, there is very lack of study dealing with the idea of efficient NH_3 production from LRC, especially the integrated one. Inaba et al. (2000) studied the

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possible utilization of heat from nuclear power for coal gasification to produce NH_3. However, building nuclear reactor is economically infeasible, especially near to the coal mining. In addition, Habgood et al. (2015) conducted a techno-economic analysis on three different technologies for producing NH_3 from LRC. However, their systems are based on conventional heat recovery system without paying enough attention on the exergy recovery. As the result, the evaluated systems show no sufficient economic feasibility.
This study focuses mainly on the proposal of integrated system covering LRC drying, coal direct chemical looping, NH_3 synthesis, N_2 production and power generation. The proposed system is developed based on the principles of exergy recovery and process integration, hence, the exergy loss throughout the integrated system can be minimized and high total energy efficiency can be achieved.

2. Modelling and calculation

2.1 Conceptual modelling

Figure 1 shows the conceptual diagram of the proposed integrated-system of NH_3 production from LRC. There are five main continuous units involved: LRC drying, coal direct chemical looping, N_2 production (air separation), NH_3 synthesis, and power generation. Raw LRC is initially dried to low moisture content and subsequently ground to very small and uniform particle size. Pulverized dried-LRC is then fed to chemical looping unit which consist of three circulated reactors: reducer, oxidizer and combustor. In this unit, LRC is decarbonized and CO_2, H_2, H_2O and heat are produced. On the other hand, N_2 production (air separation) unit is also introduced to produce N_2 which is required for NH_3 production. The produced H_2 and N_2 from chemical looping and N_2 production units, respectively, are reacted in the NH_3 synthesis unit producing NH_3. In addition, the heat generated in chemical looping and NH_3 synthesis units are recovered for power generation utilizing combined cycle system.
To achieve high total energy efficiency in the integrated system, exergy recovery and process integration technologies are employed during process modelling. The former focuses on each process unit, while the latter deals with the utilization of unrecoverable energy/heat in any process unit to other units. The concept of exergy recovery has been previously studied in the literature (Kansha et al., 2013) and applied in some industrial cases including biomass drying (Liu et al., 2012), coal drying (Liu et al., 2013) and H_2 production (Aziz et al., 2016b).

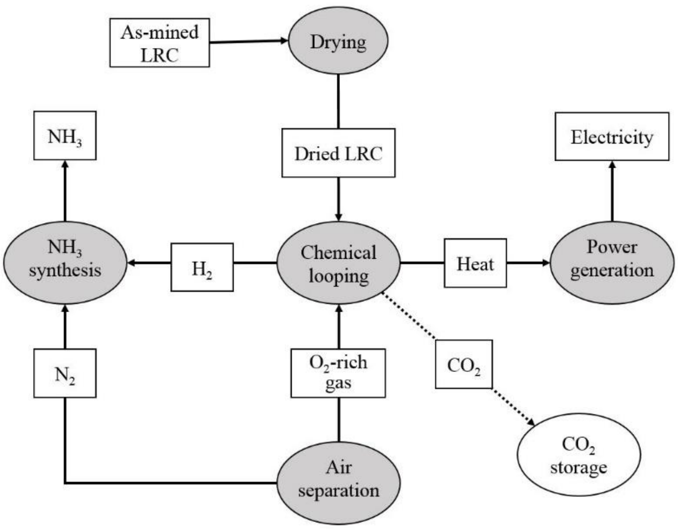

Figure 1: Conceptual block flow diagram of the proposed integrated-system converting LRC to NH_3.

2.2 Process flow diagram and calculation

Figure 2 shows the process flow diagram of the proposed NH_3 production system from LRC. LRC drying is basically modelled based on the previously available work (Aziz et al., 2014). In this study, with the consideration of low price, excellent stability and reactivity, and strong tolerance to the pollutants inherently brought by LRC (Aziz et al., 2017), iron oxide is selected as oxygen carrier circulated among the reactors in chemical looping unit. In reducer of chemical looping unit, LRC reacts with the iron oxide producing CO_2 and steam. The reduced iron oxide is then flowing to oxidizer for having reaction with steam producing H_2. The produced H_2 and excess steam are exhausted from the oxidizer and then separated after condensation. In addition, the iron oxide is then oxidized in combustor with O_2-rich gas mainly coming from N_2 production (air separation) unit. A cryogenic N_2

production is adopted in this study. The produced CO_2 is going to further sequestration. On the other hand, highly-pure H_2 is going to NH_3 synthesis unit for NH_3 production. Haber-Bosch process is adopted to react N_2 and H_2 with consideration of its well-proven and widely-adopted application.

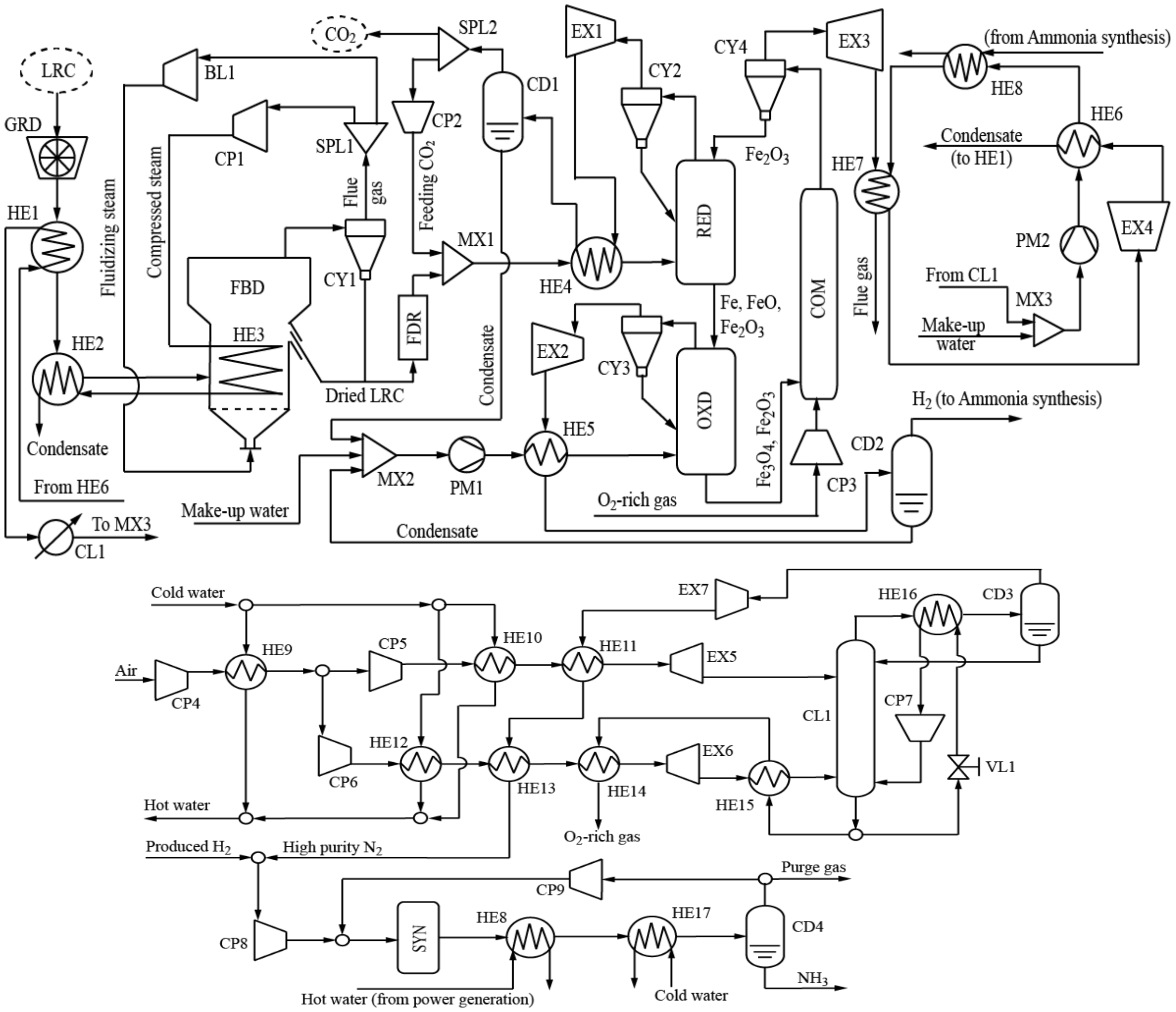

Figure 2: Process flow diagram of proposed NH_3 production system from LRC.

Table 1 shows the properties of used LRC and assumed conditions during process evaluation. Process modelling and calculation is conducted using a steady state process simulator SimSci Pro/II (Schneider Electric Software, LLC.). In addition, the reactions occur in each reducer, oxidizer and combustor of chemical looping are represented in Reactions Equ(1-7), (8-9), and (10).

$$LRC \rightarrow volatiles\ (C_xH_yO_z) + char\ (C) \quad (1)$$

$$C_{1.62}H_{4.66}O_{1.66} + 3.91Fe_2O_3 \rightarrow 7.82FeO + 1.62CO_2 + 2.33H_2O \quad (2)$$

$$C + 2Fe_2O_3 \rightarrow 4FeO + CO_2 \quad (3)$$

$$C + H_2O \rightarrow CO + H_2 \quad (4)$$

$$C + CO_2 \rightarrow 2CO \quad (5)$$

$$FeO + CO \rightarrow Fe + CO_2 \quad (6)$$

$$FeO + H_2 \rightarrow Fe + H_2O \quad (7)$$

$$Fe + H_2O \rightarrow FeO + H_2 \quad (8)$$

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2 \quad (9)$$

$$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3 \quad (10)$$

Table 1: LRC properties and assumed conditions during process calculation

Unit	Properties	Value
Drying	LRC initial moisture (wt% wb)	65.5
	LRC ultimate analysis (wt% db)	C: 66.7; H: 4.7; O: 26.6; S: 0.3
	Wet LRC flow rate (t h^{-1})	100
	Target moisture content (wt% wb)	10
Chemical looping	Reduction temperature (°C)	800
	Basic operating pressure (MPa)	3.0
NH_3 synthesis	Operating temperature (°C)	500
	Operating pressure (MPa)	20
	Conversion rate (%)	98
	Catalyst (-)	Iron-oxide base with K_2O and Al_2O_3
N_2 production	Column number of stages (-)	48
	Top tray pressure (kPa)	540
Power generation	Gas turbine maximum inlet temperature (°C)	1,300
	Steam turbine maximum inlet temperature (°C)	700
	Minimum vapour quality at steam turbine outlet (-)	0.9
Others	Min. temperature approach in heat exchanger (°C)	10
	Adiabatic efficiency of compressor and pump (%)	87
	Polytrophic efficiency of turbine (%)	90

3. Results and discussion

In this study, the effects of target moisture content during LRC drying, operating pressure in chemical looping, and carbon conversion during reduction process are evaluated in terms of the total energy conversion efficiency. As general results, the proposed integrated system shows very high total energy conversion efficiency.

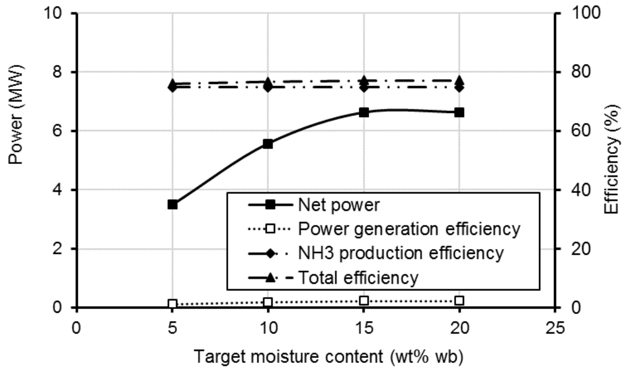

Figure 3: The effect of target moisture content in drying to the generated power and total energy conversion efficiency.

Figure 3 shows the effect of target moisture content in LRC drying to the generated power and total energy conversion efficiency. In general, the net generated power increases following the increase of target moisture content during drying, although no significant change can be observed. Numerically, the net generated power increase from 3.5 MW (target moisture content of 5 wt%) to 6.6 MW (target moisture content of 20 wt%). In addition, the total energy efficiency including power and produced NH_2 also increases from 76.0% to 77.1%, respectively. However, target moisture content has no significant effect to both H_2 and NH_3 production. Target moisture content effects the required drying temperature. Basically, lower target moisture content requires high temperature of drying. As the result, the compression work increases accordingly.

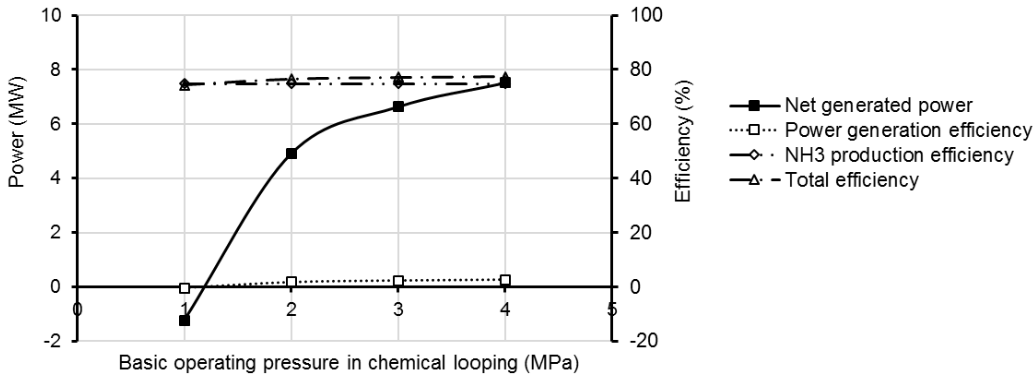

Figure 4: The effect of operating pressure in chemical looping unit to the generated power and total energy conversion efficiency.

Figure 4 shows the effect of operating pressure during direct chemical looping to generated power and total energy conversion efficiency. Higher operating pressure in chemical looping leads to higher generated power, therefore, the net generated power increases significantly. In case that the operating pressure is 1 MPa, net generated power shows a negative value, which is -1.2 MW, as well as the power generation efficiency. This means that the system is lack of power and, hence, requires power supply from the outside of system. As the operating pressure is increased, the system becomes more self-reliance in terms of power. Operating pressure during chemical looping influences strongly the compressors, pumps and turbines, especially in the chemical looping unit. The highest change of power generation was achieved in the expander after oxidizer, EX2, in which the pump work required for supplying the water, PM1, has no significant increase.

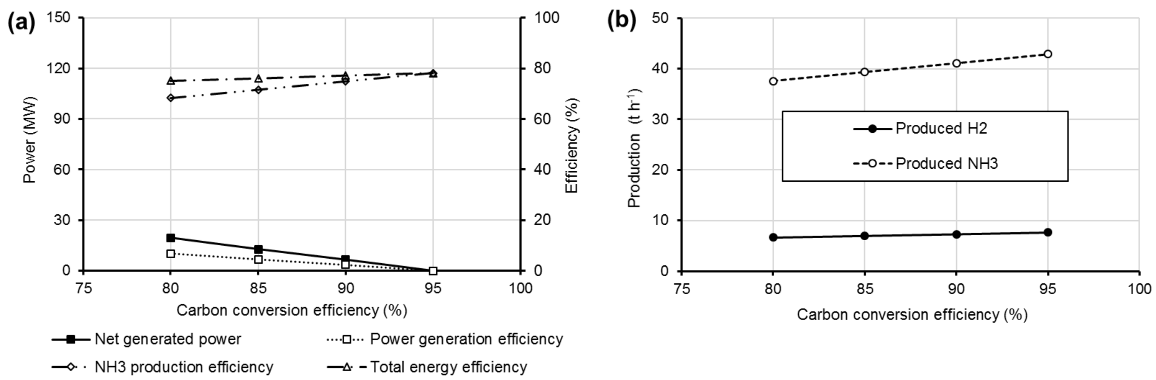

Figure 5: The effect of carbon conversion efficiency in reducer: (a) to the generated power and total energy conversion efficiency, and (b) produce H_2 and NH_3.

Figure 5 shows the effect of carbon conversion efficiency in reducer to the generated power, total energy efficiency, and produced amount of H_2 and NH_3. Carbon conversion efficiency strongly influences both the generated power and produced H_2, as well as NH_3. High carbon conversion efficiency in reducer leads to the lower generated power and power generation efficiency, but higher NH_3 production and total energy efficiencies. Numerically, the generated power decreased from 6.8 MW to 0.02 MW when the carbon conversion efficiency increased from 80% to 95%, respectively. On the other hand, both NH_3 production and total energy efficiencies increased from 68.3% and 75.1% to 78.0% and 78.1%. In addition, the produced H_2 and NH_3 increased from 6.6 t h^{-1} and 37.5 t h^{-1} to 7.6 t h^{-1} and 42.9 t h^{-1}, correspondingly. Lower carbon conversion in reducer leads to high amount of remaining carbon to be combusted in the combustor.

4. Conclusion

An integrated system to produce NH_3 from LRC consisting of LRC drying, direct chemical looping, N_2 production, NH_3 synthesis, and power generation has been proposed and modelled. In addition, combination of exergy recovery and process integration is also applied to achieve high total energy conversion efficiency, due to minimum exergy loss throughout the integrated system. Some operating parameters including target moisture content in drying, operating pressure in chemical looping unit and carbon conversion efficiency in reducer are evaluated in terms of their influences to generated power and NH_3 production. Both target moisture content in drying and operating pressure in chemical looping influences strongly the generated power, although show no significant impact to NH_3 production. Furthermore, the carbon conversion efficiency in reducer strongly effects both power generation and NH_3 production. In general, the proposed integrated-system shows very high total energy efficiency, which is about 75 %, including both power and NH_3.

Acknowledgments

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References

Aziz M., Oda T., Kashiwagi T., 2014, Energy-efficient low rank coal drying based on enhanced vapor recompression technology, Drying Technology, 32, 1621-1631.

Aziz M., Oda T., Kashiwagi T., 2015, Clean hydrogen production from low rank coal: Novel integration of drying, gasification, chemical looping, and hydrogenation, Chemical Engineering Transactions, 45, 613-618.

Aziz M., Juangsa F.B., Kurniawan W., Budiman B.A., 2016a, Clean co-production of H_2 and power from low rank coal, Energy, 116, 489-497.

Aziz M., Oda T., Morihara A., 2016b, Energy-efficient co-production of hydrogen and power from brown coal employing direct chemical looping, Chemical Engineering Transactions, 52, 721-726.

Aziz M., Zaini I.N., Oda T., Morihara A., Kashiwagi T., 2017, Energy conservative brown coal conversion to hydrogen and power based on enhanced process integration: Integrated drying, coal direct chemical looping, combined cycle and hydrogenation. International Journal of Hydrogen Energy, 42, 2904-2913.

Giddey S., Badwal S.P.S., Kulkarni A., 2013, Review of electrochemical ammonia production technologies and materials, International Journal of Hydrogen Energy, 38, 14576-14594.

Habgood D.C.C., Hoadley A.F.A., Zhang L., 2015, Techno-economic analysis of gasification routes for ammonia production from Victorian brown coal, Chemical Engineering Research and Design, 102, 57-68.

Kansha Y., Kotani Y.Aziz M., Kishimoto A., Tsutsumi A., 2013, Evaluation of a self-heat recuperative thermal process based on thermodynamic irreversibility and exergy, Journal of Chemical Engineering of Japan, 46, 87-91.

Liu Y., Aziz M., Kansha Y., Tsutsumi A., 2012, Drying energy saving by applying self-heat recuperation technology to biomass drying system, Chemical Engineering Transactions, 29, 577-582.

Liu Y., Aziz M., Kansha Y., Tsutsumi A., 2013, A novel exergy recuperative drying module and its application for energy-saving drying with superheated steam, Chemical Engineering Science, 100, 392-401.

Tanabe Y., Nishibayashi Y., 2013, Developing more sustainable processes for ammonia synthesis, Coordination Chemistry Reviews, 257, 2551-2564.