

Journal Pre-proofs

Full Length Article

Energy and economic analysis of a hydrogen and ammonia co-generation system based on double chemical looping

Xin Pan, Jingjing Ma, Xiude Hu, Qingjie Guo

PII: S1004-9541(20)30617-0
DOI: <https://doi.org/10.1016/j.cjche.2020.10.007>
Reference: CJCHE 2010

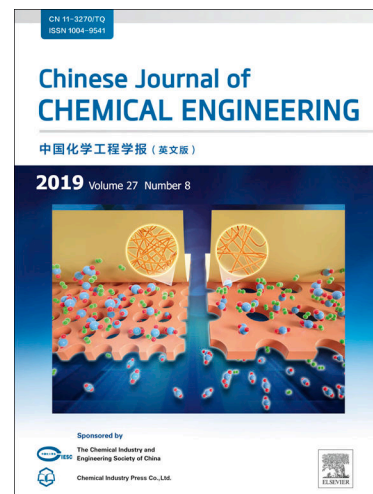
To appear in: *Chinese Journal of Chemical Engineering*

Received Date: 4 August 2020
Revised Date: 9 October 2020
Accepted Date: 16 October 2020

Please cite this article as: X. Pan, J. Ma, X. Hu, Q. Guo, Energy and economic analysis of a hydrogen and ammonia co-generation system based on double chemical looping, *Chinese Journal of Chemical Engineering* (2020), doi: <https://doi.org/10.1016/j.cjche.2020.10.007>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 The Chemical Industry and Engineering Society of China, and Chemical Industry Press



**Energy and economic analysis of a hydrogen and ammonia co-generation system
based on double chemical looping**

Xin Pan, Jingjing Ma, Xiude Hu*, Qingjie Guo*

State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering, Ningxia
University, Yinchuan, 750021, China.

*Corresponding author: Qingjie Guo

E-mail: xqjguo@qust.edu.cn

Fax/Tel: +86-951-2062323

Address: State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical
Engineering, Ningxia University, Yinchuan, 750021, China

*Corresponding author: Xiude Hu

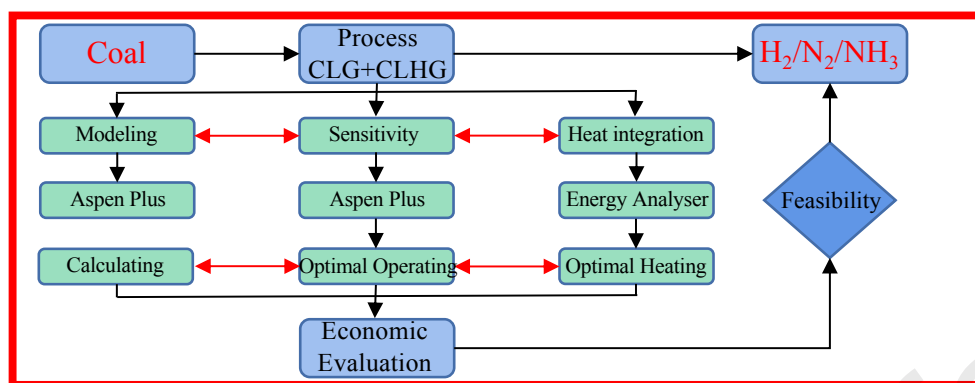
E-mail: xiude_hu@163.com

Address: State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical
Engineering, Ningxia University, Yinchuan, 750021, China

Abstract:

In this work, a model of hydrogen production by double chemical looping is introduced. The efficiency benefit obtained was investigated. The chemical looping hydrogen generation unit is connected in series to the downstream of a chemical looping gasification unit as an additional system for 100 MW·h coal gasification, with the function of supplementary combustion to produce hydrogen. Using Aspen Plus software for process simulation, the production of H₂ and N₂ in the series system is higher than that in the independent Chemical looping gasification and Chemical looping hydrogen generation systems, and the production of hydrogen is approximately 25.63 % and 12.90 % higher, respectively; The study found that when the gasification temperature is 900 °C, steam-carbon ratio is 0.84 and oxygen-carbon ratio is 1.5, the hydrogen production rate of the system was the maximum. At the same time, through heat exchange between logistics, high-pressure steam at 8.010×10⁴ kg·h⁻¹ and medium-pressure steam at 1.101×10⁴ kg·h⁻¹ are generated, and utility consumption is reduced by 61.58 %, with utility costs decreasing by 48.69 %. An economic estimation study found that the production cost of ammonia is 108.66 USD·(t NH₃)⁻¹. Finally, cost of equipment is the main factors influencing ammonia production cost were proposed by sensitivity analysis.

Keywords: Chemical looping, Hydrogen, Ammonia, Energy evaluation, Economic evaluation



Graphical abstract

Highlights:

1. A new process of double chemical looping is proposed.
2. N₂ utilization can significantly improve the system economical efficiency.
3. Technoeconomic analysis of double chemical looping is performed.
4. Cost of equipment is very sensitive to the NH₃ cost.

1. Introduction

Emissions of global greenhouse gases are accelerating because of the growing demand for and consumption of fossil fuels as the source of hydrogen. Without action to curb CO₂ emissions, it is impossible to limit global average temperature increases to 2 °C above pre-industrial levels [1]. Facing this problem, the scientists have been carrying out a series of studies to improve environmental conditions. In terms of energy, renewable energy sources such as biomass, solar, wind and tidal energy have been vigorously developed [2,3].

Chemical looping technology (CLT) is a new type of chemical transformation and energy utilization technology [4-6]. As a flow bridge between the oxidation reactor and reduction reactor, oxygen carriers can realize gasification, indirect contact of multiple reactants and direct separation of products by utilizing the oxygen and heat carrying capacity of metal oxides [7]. This technology breaks through the traditional coal gasification technology requiring an air separation device, achieves CO₂ capture and controls the generation of NO_x to obtain electric energy, syngas, hydrogen, *etc.* In CLT, chemical looping combustion (CLC) is relatively mature and has formed semi-industrial scale units, such as the 1 MW_{th} CLC unit at Darmstadt University of Technology (TUD, Germany) [8] and the 4 MW_{th} CLC boiler at Chalmers University of Technology (CUT, Sweden) [9]. However, chemical looping gasification (CLG) is still in the stage of experimental and simulation calculations, which is also in the primary stage for the preparation of syngas and further production of chemicals. Therefore, it is necessary and urgent to simulate CLG of the MW level to produce hydrogen or chemicals.

Syngas and hydrogen are the key ingredients for the production of valuable chemicals, and hydrogen is an important source of clean energy. Therefore, the production of syngas and hydrogen is

crucial. The main purpose of CLG is to produce hydrogen and syngas, which provides feedstock for downstream chemical processes. Since the introduction of chemical looping technology, many scientists have modeled and simulated the process of chemical looping hydrogen and syngas production, studied the influence of different conditions on the gasification process and provided operating parameters for the amplification process. Zhang *et al.* [10] simulated the 10 MW-h coal-based CLG process, sought and optimized the operational parameters of the a pilot gasification plant, and analysed their effects on the product distribution and system; Through experiments and process simulation, Nadgouda *et al.* [11] studied the co-production of syngas and hydrogen by Cu-Fe oxygen carriers during chemical looping reforming. Wang *et al.* [12] used the Gibbs free energy minimization method to conduct thermodynamic analysis of the combined production of syngas and hydrogen by CLG and chemical looping hydrogen generation (CLHG) and obtained the optimal parameters of syngas and hydrogen. Ge *et al.* [13] designed a new generation system integrating biomass-based integrated gasification combined cycle (BIGCC) and CLG and used Aspen Plus software to simulate the whole process of biomass gasification, gas purification, and heat recovery steam generator (HRSG) and gas/turbine. Wijayanta *et al.* [14] simulated an integrated system consisting mainly of hydrothermal gasification (HTG), chemical looping, N₂ production, NH₃ synthesis and power generation, but the nitrogen source of ammonia synthesis is still from the air separation device, which makes the ammonia production cost still high. Muhammad Aziz *et al.* [15] proposed a highly energy efficient integrated system co-production H₂ and power from coal, and stored the H₂ through chemical organic hydrides. The research process focuses on heat circulation or exergy recovery without process design, calculation and operation parameter setting. It can be seen that most researchers focus on the simulation of hydrogen production, syngas or power generation, but there is

less continuous simulation research on chemical products after gasification and less economic analysis on the system. Therefore, more efforts are still needed to study the simulation of chemical production by chemical looping gasification.

The process of double chemical looping gasification to produce hydrogen and co-production of ammonia was thoroughly studied through economic analysis. CLG is a gasification process to produce hydrogen, while CLHG is a secondary supplementary combustion process to produce hydrogen, which can convert all carbon sources into hydrogen with higher industrial value. First, the dominating parameters affecting the system are analysed and discussed through sensitivity analysis. Second, with the help of Aspen Energy Analyzer software for energy analysis, process thermal integration of the system is carried out to achieve maximum heat recovery. Finally, an economic evaluation of the system is conducted to demonstrate the feasibility of the process, and efforts are made to explore the process of efficient clean utilization of coal and other solid fuels (such as biomass and solid waste).

2. Process description

With coal as raw fuel, the double chemical looping system of hydrogen and ammonia co-generation system includes CLG, water-gas shift (WGS) of crude syngas, CLHG, synthetic ammonia production and steam system. A schematic diagram of the entire system is shown in Fig.1.

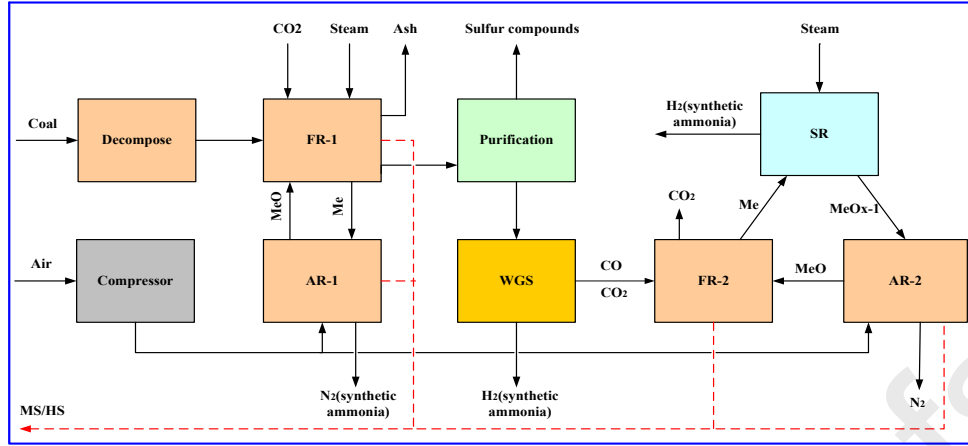
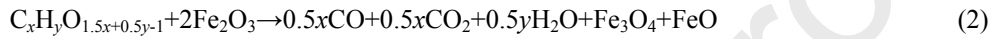
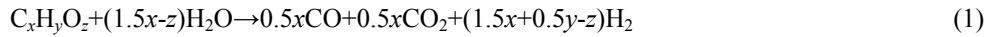


Fig. 1. Schematic of double chemical looping system of hydrogen and ammonia co-generation system

2.1 Chemical looping gasification

Coal gasification is the leading and important part of the whole system. First, solid fuel is thermally decomposed in a fuel reactor (FR-1) and then reacts with water vapour or CO_2 (as a gasifying and fluidizing agent) and oxygen carrier (OCs) Fe_2O_3 to obtain crude syngas and ash (shown in Eqs. (1), (2), and (3)), where fresh oxygen carrier Fe_2O_3 is principally reduced to Fe_3O_4 with a lower valence state under the stream atmosphere [16-18], as shown in the reaction Eq. (4). A cyclone separator and magnetic properties of iron-based oxygen carriers were used to separate the reduced OCs from the gas phase and ash [19-21]. In the air reactor (AR-1), due to the limitation of the structure and properties of Fe-based oxygen carriers, the oxidation reaction Eq. (5) occurred at the maximum oxidation temperature of $1050\text{ }^\circ\text{C}$ to obtain oxygen atoms and carry out oxygen carrier regeneration [22]. Moreover, in this process, efficient separation of N_2 gas can be achieved, which greatly reduces the N_2 enrichment cost compared with air separation [5,14,23] and provides raw materials for downstream ammonia synthesis.

In FR-1:



In AR-1 and in AR-2:



2.2 Rich hydrogen system

The content of H_2 in syngas can be increased by two methods. First, the WGS reaction occurs in the water-gas shift reactor (R-WGS), where approximately 70 % of the water vapour in the synthetic gas is converted into H_2 , under the condition of normal pressure, 250 °C and no additional water vapour

input. At this point, the carbon monoxide in the syngas is partially converted into carbon dioxide, and the reaction occurs as shown in Eq. (6). Second, unconverted carbon monoxide passes through CLHG to produce heat and a small amount of H₂.

In FR-2:



In SR:



CLHG is a new technology that produces H₂ by taking advantage of oxygen carrier (OCs) circulation with different redox states [24-29]. Under normal conditions, a CLHG system consists of three reactors: a fuel reactor (FR-2), a steam reactor (SR), and an air reactor (AR-2). In FR-2, oxygen-rich Fe₂O₃ is reduced to FeO by CO, and CO is almost completely oxidized to CO₂ (as shown in Eq. (7)), which is directly captured and stored through cooling; In SR, FeO is oxidized by water vapour to generate the H₂ and the intermediate product Fe₃O₄, as shown in Eq. (8). Moreover, H₂ can be directly and easily obtained by condensation of unreacted water vapour; In AR-2, Fe₃O₄ from SR reacts with air to form Fe₂O₃ and N₂, as shown in Eq. (5). Therefore, the main effect of CLHG is that the chemical looping combustion of unconverted CO to increases the carbon capture rate and produces hydrogen to improve the economics of this process.

2.3 Ammonia synthesis

In the process of ammonia synthesis, hydrogen and nitrogen are compressed by a compressor to

the desired pressure, and the catalyst is used to catalyse the synthesis of ammonia (Eq. 9). It is well known that the low-pressure method is the most core technology in the actual production of ammonia synthesis, with relatively low requirements on the actual equipment and simple practical operation [14,30]. Therefore, the low-pressure method is chosen. Although the reaction was carried out under high temperature and pressure, the NH_3 content was only 10 %-20 %. Therefore, the unreacted N_2 and H_2 were basically recycled back to the reactor of NH_3 (R- NH_3).

In R- NH_3 :



The superiority of hydrogen and ammonia co-generation systems based on double chemical looping is summarized below: (1) Oxygen required in the gasification process is introduced by OCs, which removes complicated air separation units (ASU) and saves equipment investment. Xiang *et al.* [31] proposes a novel process of coke-oven gas to H_2 and NH_3 by integrating chemical looping hydrogen generation and pressure swing adsorption technology (CG_{PSA} -CLHA). However, CG_{PSA} -CLHA still introduces ASU. (2) Since oxygen and fuel are not in direct contact, the internal reaction temperature of FR is obviously lower than that of conventional combustion, which inhibits the formation of pollutants containing sulfur and nitrogen, and brings convenience to the subsequent purification process [7,32]; and (3) Edrisi *et al.* [33] evaluated the three reactors of chemical looping (TRCL) technology for the production of H_2 , N_2 , and CO_2 from methane. TRCL technology is a independent CLHG process. CLG and CLHG are connected in series to generate more hydrogen, to achieve maximum carbon source transformation, to realize low energy consumption and high-efficiency CO_2 capture.

3. Methodology

In this study, Ningxia YangChang's bitumite (NX) in the Ningxia Hui Autonomous Region of China with a power level of 100 MW·h was selected as the solid fuel, and its proximate analysis and ultimate analysis were shown in Table 1. The steady-state process simulation software Aspen Plus version 9.0 was used for modelling and calculation. According to the Aspen Physical Property System Guide, Peng-Robinson was selected as the Property Method, a collection of methods and models required in simulation calculations, to estimate the energy balance and material balance.

Table1. Proximate analysis and ultimate analysis of NX

Sample	Proximate analysis/wt%				Ultimate analysis/wt%					LHV/ MJ·kg ⁻¹
	Moisture	Ash	Volatiles	Fixed Carbon	C	H	N	S	O	
NX	5.18	4.56	26.95	63.31	77.6	5.16	1.46	0.46	10.77	24.71

According to the characteristics of different models and the experience of predecessors, a model suitable for the system was chosen. The reactors FR, AR and SR in the CLG and CLHG processes were all RGibbs modules; chemical equilibrium and phase equilibrium were calculated by minimizing the Gibbs free energy [34,35]. However, a stoichiometric reactor was used in the coal pyrolysis process. The REquill reactor module was introduced into the WGS system, where chemical and phase equilibria occurred simultaneously [36]; the RGibbs module was also selected for simulation calculation of the ammonia synthesis system. The selection of required modules, important process design parameters and several assumptions used in the modelling are shown in Table 2. The corresponding design parameters were input in Aspen Plus, and the whole system was run and calculated. Ultimately, the correct simulation results were obtained, as discussed in detail below.

Table 2. Unit Operation Models and design Specifications

Unit Operation	Model	Key specifications
CLG	RStoic, RGibbs, HeatX, Sep, Mixer, Flash2,	FR-1: Operation condition: Calculate phase equilibrium and chemical equilibrium Operation temperature: 900 °C Operation pressure: 0.1 MPa Gasifying and fluidizing agent: steam AR-1: Operation condition: Calculate phase equilibrium and chemical equilibrium Operation temperature: 1050 °C Operation pressure: 0.1 MPa
R-WGS	REquill,HeatX, Sep, Flash2	R-WGS: Operation duty: 0 kW Operation pressure: 0.1 MPa Feed temperature: 200 °C
CLHG	RGibbs, HeatX, Sep, Mixer, Flash2,	FR-2: Operation condition: Calculate phase equilibrium and chemical equilibrium(Identify possible products) Operation temperature: 900 °C Operation pressure: 1 MPa SR: Operation condition: Calculate phase equilibrium and chemical equilibrium Operation pressure: 1 MPa [35] AR-2:

		Operation condition: Calculate phase equilibrium and chemical equilibrium
		Operation temperature: 1050 °C
		Operation pressure: 1 MPa
Ammonia synthesis	RGibbs,	R-NH ₃ :
	MCompr,	Operation condition: Calculate phase equilibrium and chemical equilibrium
	HeatX, Mixer,	Operation temperature: 450 °C
	Flash2,	Operation pressure: 15 MPa [37]

4. Results and discussion

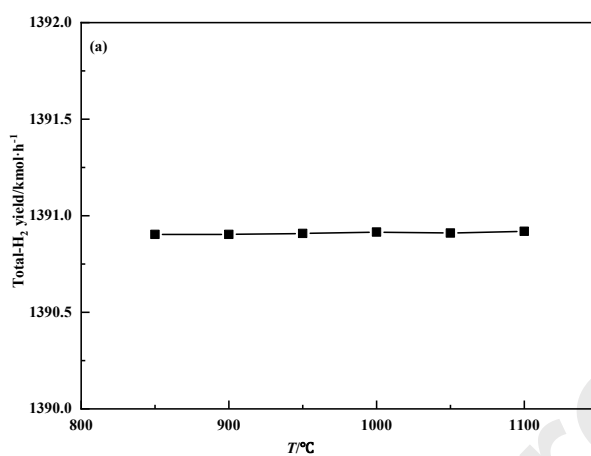
4.1 Sensitivity analysis

Through sensitivity analysis, the optimal operating parameters are found to achieve system efficiency, which paves the way for the next step of economic analysis.

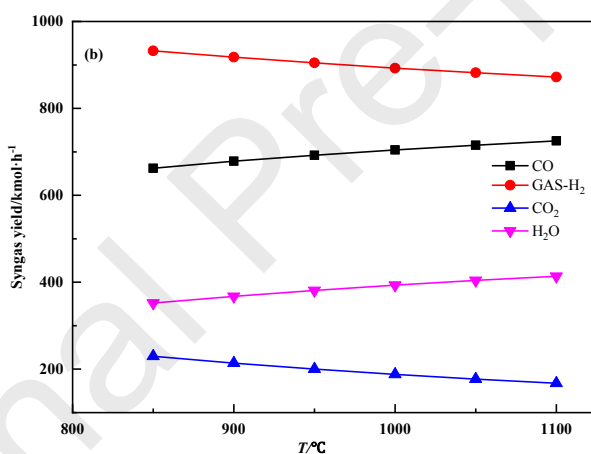
4.1.1 Effect of gasification temperature

Fig.2 shows the influence curves of gasification temperature on the yield of total hydrogen (Total-H₂), syngas, and hydrogen production in WGS and CLHG units. As shown in Fig.2 (a), with increasing temperature, the Total-H₂ yield basically remained stable. The Total-H₂ is produced by three cells, as shown in Fig.2 (b) and Fig.2 (c); when the temperature increases, the production of gasification hydrogen (Gas-H₂) decreases. In contrast, the CO content increases. Therefore, more CO enters the WGS and CLHG units and generates more hydrogen output the WGS unit (WGS-H₂) and hydrogen output the CLHG unit (SR-H₂). In this system, CLHG acts as a complementary combustion process to produce H₂, as long as steam-carbon ratio (S/C) and oxygen-carbon ratio (O/C) are fixed, regardless of what happens between CO and H₂ in the syngas. Therefore, the Total-H₂ basically does

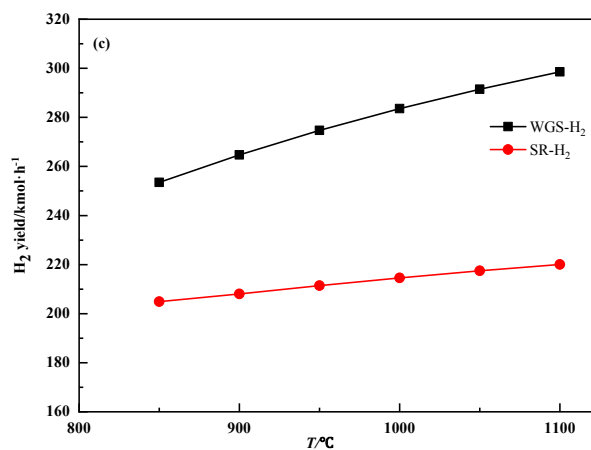
not change with the temperature and the operating temperature of the gasification reactor ranges from 850 °C to 1100 °C.



(a) The yield of total H₂

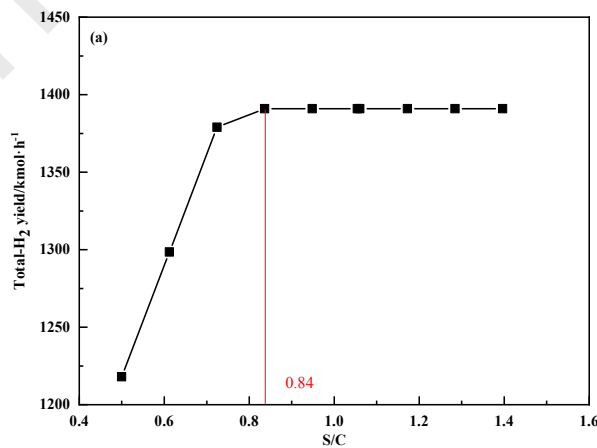


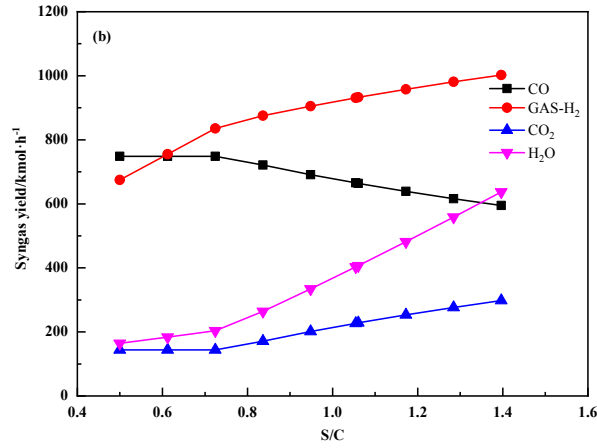
(b) The yield of syngas



(c) The yield of H₂**Fig. 2. Effects of gasification temperature (T) on various indexes****4.1.2 Effect of the steam-carbon ratio**

As shown in Fig.3 (a), from $S/C=0.5-1.4$, the Total-H₂ production first increases and then basically remains unchanged. As shown in Fig.3 (b) and Fig.3 (c), Gas-H₂ and WGS-H₂ both increase with increasing steam content. However, the yield of SR-H₂ shows a downward trend. Meanwhile, at $S/C < 0.94$, the content of SR-H₂ is higher than that of WGS-H₂, but later, it is the opposite. The reason is because when S/C is small, the water vapour content in the WGS unit is lower and less CO is converted. Most CO in the syngas goes into the CLHG unit to be burned to produce hydrogen. When $S/C > 0.94$, due to the increase in water content, most of the CO in WGS is converted into hydrogen, while only a handful of CO enters CLHG unit. Although steam is the main source of H₂, a higher amount will increase the thermal load of CLG. It is expected that the water vapour content should be reduced as much as possible so that the maximum H₂ amount can be produced. Therefore, $S/C=0.84$ is optimal.

**(a) The yield of total H₂**



(b) The yield of syngas

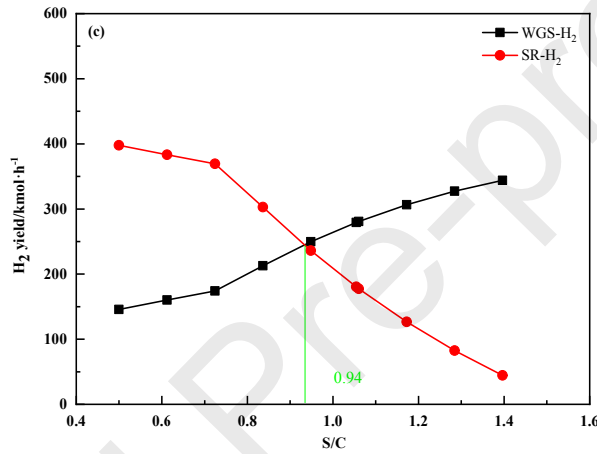
(c) The yield of H₂

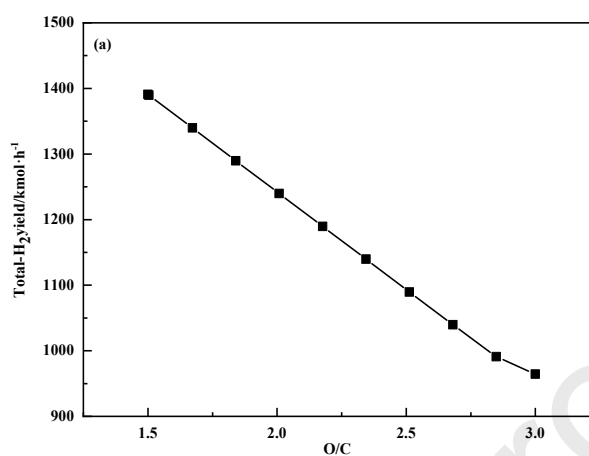
Fig. 3. Effects of stream carbon ratio (S/C) on various indexes

4.1.3 Effect of the oxygen-carbon ratio

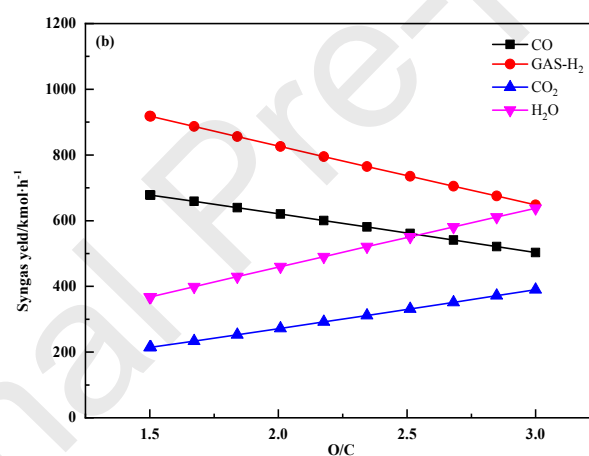
As shown in Fig.4 (a), when O/C changed from 1.5 to 3.0, the Total-H₂ yield decreased from 1404 kmol·h⁻¹ to 979 kmol·h⁻¹, showing a negative correlation. With an increase in the O/C ratio, the yield of CO and H₂ in syngas decreases, while the content of CO₂ and H₂O increases (Fig.4 (b)). As can be seen from Fig.4 (c), the yield of WGS-H₂ and SR-H₂ changes with O/C in an opposite trend. Moreover, the hydrogen production capacity of the CLHG unit is smaller than that of the WGS unit. Due to the increase in the O/C ratio, the decrease in CO in syngas and the increase in water vapour,

together with the further conversion in the WGS unit, increasingly less CO enters the CLHG unit.

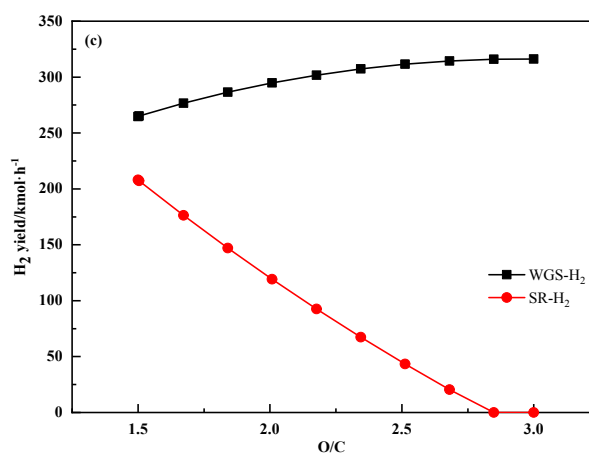
When at $O/C > 2.85$, almost no CO enters the device.



(a) The yield of total H₂

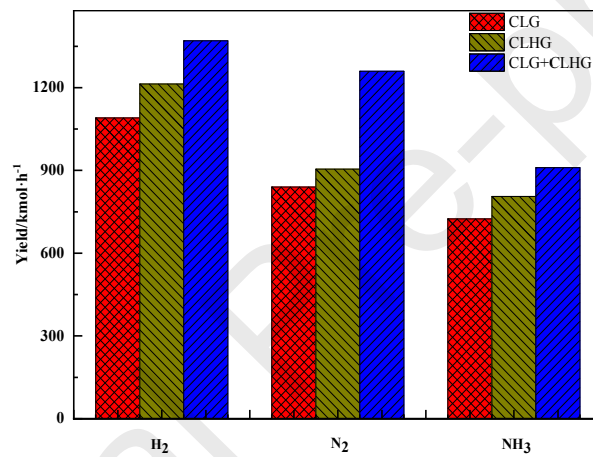


(b) The yield of syngas



(c) The yield of H_2 **Fig. 4. Effects of oxygen carbon ratio (O/C) on various indexes**

Meanwhile, the hydrogen yield in the CLG and CLHG processes with the same feed was calculated and compared with the cascade system, as shown in Fig.5. The separate CLG and CLHG systems with the same feed and operating parameters produce less H_2 , N_2 , and NH_3 than the coupled system, with the CLG system presenting the lowest values. Compared with CLG and CLHG, the serial system produced 25.63 % and 12.90 % more hydrogen and 49.96 % and 39.22% more N_2 , respectively.

**Fig. 5. Different system product yields**

In conclusion, the gasification temperature, S/C and O/C affect the downstream WGS and CLHG units by affecting the content of CO and steam in the syngas. The obtained principle is that the gasification temperature hardly affects the Total- H_2 yield. However, with an increase in S/C, the Total- H_2 yield presents an upward trend. After reaching a certain value, S/C has no effect on the total- H_2 yield. In contrast, an increase in O/C will cause the total- H_2 production rate to plummet. The operating conditions were determined to be 900 °C, S/C=0.84, O/C=1.5. The Gas- H_2 content accounts for 63.97 % of the total hydrogen, while WGS- H_2 and SR- H_2 respectively account for 15.63 % and

20.40 %, respectively. It is known that the main hydrogen-producing unit of the system is CLG; however, CLHG plays a role in reburning to produce hydrogen.

4.2 Heat integration and energy analysis

The heat transfer of the whole system includes heat transfer between logistics and equipment. The material flows coming out of FR, AR and R-NH₃ all have high temperatures, some as high as 1050 °C, such as the flow coming out of AR-1 and AR-2. However, water entering the FR-1 and SR reactors is only heated to the reaction temperature. To improve energy utilization and save resources and energy, heat exchange and steam generation between streams in the system are considered to achieve maximum heat recovery and improve the thermodynamic efficiency of the process as much as possible. Steam generation is recommended by the software for low-pressure (125 °C) medium-pressure (175 °C) and high-pressure (250 °C) steam.

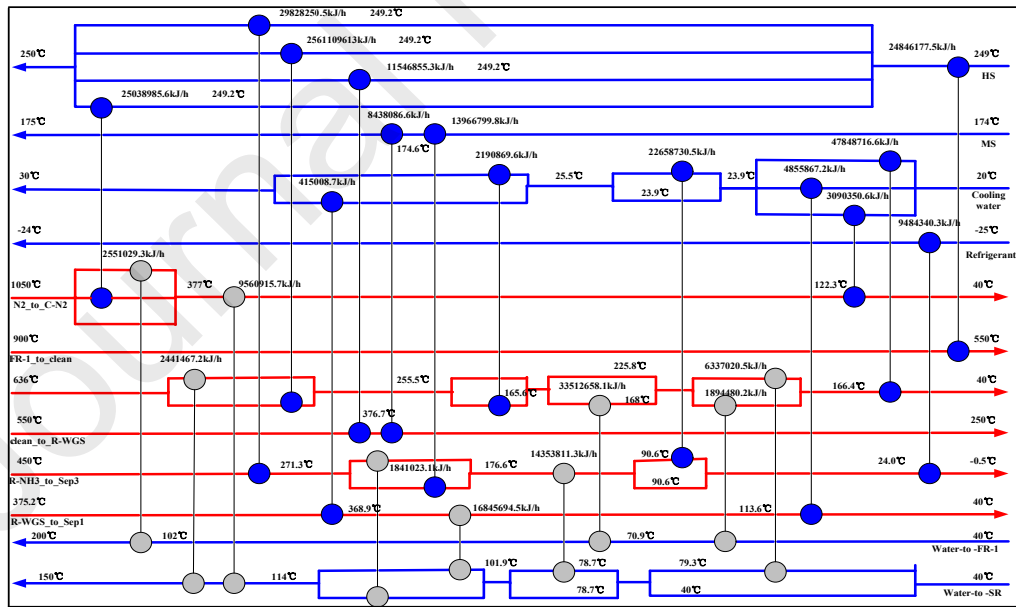


Fig. 6. Heat Exchange Network of the system

Fig.6 shows the heat exchange network diagram recommended by the software.

Through heat exchange between logistics, the water entering the FR-1 and SR reactors ultimately reached the reaction temperature, and generated high-pressure steam (HS) $8.012 \times 10^4 \text{ kg} \cdot \text{h}^{-1}$ and medium-pressure steam (MS) $1.101 \times 10^4 \text{ kg} \cdot \text{h}^{-1}$ respectively. However, no low-pressure steam (LS) was generated. Table 3 shows the thermal integration network data before and after the heat exchange, which include the utility cost index, the equipment cost index of the heat exchanger, the operating cost index and the total annual cost index. The number of heat exchangers increased to 23; likewise the equipment cost index of the heat exchanger increased by 51.09 % to 2.427×10^6 cost per second, but the utility, the operation and the total annual cost index decreased. In addition to the water entering the FR-1 and SR reactors in the system needing to be heated, other logistics need to be cooled, so the heat exchange of logistics does not require heating utilities. However, some of the equipment needs to heat transfer.

Table 3. Thermally integrated network data before and after heat exchange

Before		After	
	Cost index		Cost index
Heating (cost per second)	0.000	Heating (cost per second)	0.000
Cooling (cost per second)	5.148×10^{-2}	Cooling (cost per second)	-7.879×10^{-2}
Operating (cost per second)	5.148×10^{-2}	Operating (cost per second)	-7.879×10^{-2}
Capital (cost per second)	1.187×10^6	Capital (cost per second)	2.427×10^6
Total cost (cost per second)	6.37×10^{-2}	Total cost (cost per second)	-5.4×10^{-2}
Number of unit	6	Number of unit	23
Area/m ²	4425	Area/m ²	8306

Combined with the thermal integration between the above process logistics and the consumption of plant utilities, the consumption and cost of utilities for the overall system are analysed using the

Aspen Energy Analyzer software, as shown in Fig.7. As can be seen from Fig.7 (a), the consumption of heating utilities decreased by 52.83 %; cooling utility consumption decreased by 71.04 %; and total utilities declined from 1.90×10^5 kW to 7.31×10^4 kW after heat exchange. Approximately 61.58 % of the utility consumption was saved, so the cost of utilities was also reduced, as shown in Fig.7 (b). Heating utility costs were 38.18 % lower; cold utility costs decreased by 77.97 % and total utility costs decreased by 48.69 %.

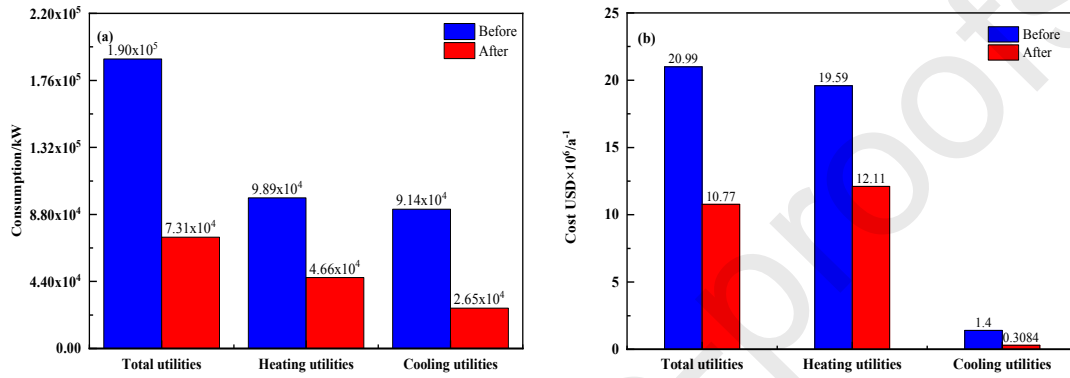


Fig. 7. Consumption and cost of system utilities before and after heat exchange

4.3 Economic evaluation

According to the previous sensitivity analysis and thermal integration of the system, the economic efficiency of the system can be maximized only when the system is operated under the optimal condition and in the most energy-saving way. Therefore, the above complex system design, sensitivity analysis and thermal integration are necessary for economic evaluation. Darmawan *et al.* [38] developed a system to convert black liquor into NH_3 by combining exergy recovery and process integration technology. But Arif Darmawan does not demonstrate the economic analysis of the integrated system, and the feasibility of the system remains to be proved. So, economic assessments are critical to assessing the overall feasibility of the proposed layout.

The cost of ammonia products (C_{NH_3}) is an essential indicator to determine the economic feasibility, which can be calculated by the following formula:

$$C_{\text{NH}_3} = \frac{\text{Total investment cost} + \text{Total Fix O \& M cost} - \text{Total sales benefit}}{m_{\text{NH}_3}/t} \quad (10)$$

Table 4. The basic economic assumptions [39-42]

Item	Assumption
Coal price	87.108 USD·t ⁻¹
Iron-based OC	90 USD·t ⁻¹
Iron-based OC lifetime	1315 h
Catalyst price	1428 USD·t ⁻¹
Ammonia price	285.6 USD·t ⁻¹
Nitrogen gas prices	114.24 USD·t ⁻¹
Annual operation time	7200 h
Plant life	25 years
Direct labor	35 persons
Average annual direct labor cost	50000 USD/person
Administrative support and overhead cost	35% form direct labor cost
Annual maintenance costs	3.5% from total installed costs
Owner's cost and contingency cost	15% of total installed cost
Land, permitting, surveying etc. cost	10% of total installed cost
Property taxes and insurance	3% of the total installed costs

Based on previous work, the basic parameters required in the calculation process are critical to the economic interest of this proposed system, as listed in Table 4. The total permanent investment is first calculated either using the Aspen Process Economic Analyzer or from cost estimates from the literature [35,43-46]. Under the designed and optimal conditions, the cost of ammonia products is 108.66 USD·(t NH₃)⁻¹. Nakaten *et al.* [47] proposed that the production cost of onshore and underground coal gaification is approximately 204.6 USD·(t NH₃)⁻¹; Demirhan *et al.* [37] pointed out that the cost of producing ammonia from natural gas and biomass is 375.41-1077.84 USD·(t NH₃)⁻¹. It can be found

that series coupling systems produce ammonia at a very low cost. Moreover, if the generated HS and MS are considered, the economic potential of such a system would be further highlighted.

In the economic evaluation process, sensitivity analysis is used to analyse and evaluate key factors, including NH_3 price, feed price or total equipment costs, etc. As shown in Fig.8, between -20% and +20% of sensitivity, NH_3 price, total equipment costs and total investment costs are the three parameters that have the greatest impact on ammonia production costs. Instead, what is interesting is that feed price and Fix Operation and Maintenance (Fix O & M) costs have very little impact, fluctuating only in the $60 \text{ USD} \cdot (\text{t NH}_3)^{-1}$ range. As the NH_3 price is determined by the market, its fluctuation is difficult to control. Therefore, it is necessary to try to reduce equipment costs and investment costs during the construction of the plant.

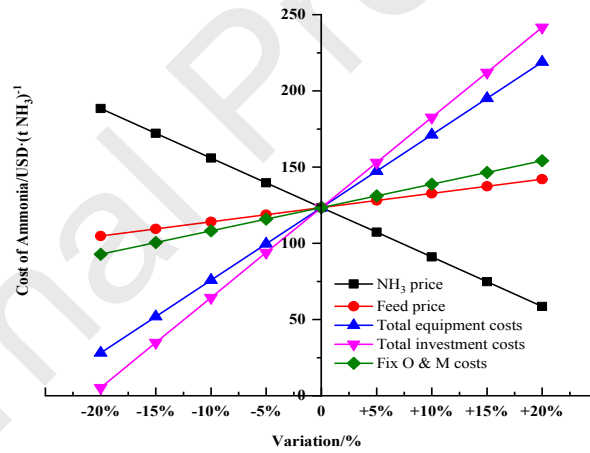


Fig. 8. Sensitivity analysis of economic feasibility

5. Conclusion

This work mainly focused on the feasibility of producing H_2 and co-producing ammonia in a series coupling system (CLG+CLHG) from an economic perspective. Finally, the economic evaluation was conducted under the conditions of optimal system, optimal operating parameters and minimal energy consumption, and the following conclusions were obtained:

(1) According to the simulation calculation, the production of H_2 and N_2 in the CLG+CLHG system is higher than that of a single independent system, such as CLG or CLHG, because CLHG, as a downstream unit, plays a role in afterburning to produce hydrogen in the whole system, while CLG is the main H_2 production unit;

(2) Regarding the influence of the key parameters of gasification temperature, S/C and O/C on the hydrogen production rate, the study shows that they affect the downstream WGS and CLHG units by affecting the CO and water vapor content in the syngas, thus controlling the total hydrogen production rate. Finally, the Total- H_2 yield reaches its maximum at a temperature of 900 °C, S/C of 0.84, and O/C of 1.5;

(3) After the design and optimization of the heat exchanger network, approximately 61.58 % of the total utility consumption was saved, so the cost of utilities was also reduced, with the total utility cost reduced by 48.69 %.

(4) The economic evaluation found that NH_3 price, total equipment costs and total investment costs were the main factors affecting C_{NH_3} , while feed price and Fix O & M costs were not significant. The specific ammonia production cost is 108.66 USD·(t NH_3)⁻¹, which is lower than that of traditional production technology and some emerging technologies.

In conclusion, the double chemical looping system not only maximizes the transformation of carbon source, but also breaks the traditional ASU to capture nitrogen source, thus greatly reducing the production cost of ammonia. This system has a very good prospect for hydrogen production and hydrides. In the future, it is necessary to combine with the actual process to obtain experimental data to provide support for scale-up.

Nomenclature

AR	air reactor
ASU	air separation units
BIGCC	biomass-based integrated gasification combined cycle
CLT	chemical looping technology
CLG	chemical looping gasification
CLHG	chemical looping hydrogen generation
C_{NH_3}	ammonia production cost, USD·(t NH ₃) ⁻¹
FR	fuel reactor
Fix O & M cost	fix operation and maintenance cost, USD
GAS-H ₂	hydrogen output the CLG unit, kmol·h ⁻¹
HRSG	heat recovery steam generator
HTG	hydrothermal gasification
HEN	heat exchange network
HS	high-pressure steam, kg·h ⁻¹
LHV	low heat value, MJ·kg ⁻¹
LS	low-pressure steam, kg·h ⁻¹
MS	medium-pressure steam, kg·h ⁻¹
NX	Ningxia Yangchang's bitumite
OC	oxygen carrier
O/C	oxygen-carbon ratio
R-WGS	water-gas shift reactor
R-NH ₃	ammonia synthesis reactor
SR	stream reactor
S/C	stream-carbon ratio
SR-H ₂	hydrogen output the CLHG unit, kmol·h ⁻¹
Total-H ₂	total hydrogen yield, kmol·h ⁻¹

TRCL	three reactors of chemical looping technology
WGS-H ₂	hydrogen output the WGS unit, kmol·h ⁻¹
WGS	water-gas shift

Acknowledgement

This work was supported by the National Key Research and Development Program of China [2018YFB0605401]; the National Natural Science Foundation of China [21868025]; and Major Program of Key Research and Development Program of Ningxia Province of China [2018BCE01002].

References

- [1] B.Su, X.J. Gao, C.D. Xiao, Interpretation of IPCC SR1.5 on cryosphere change and its impacts, *Adv. Clim. Chang. Res.*, 15 (14) (2019) 395-404.
- [2] Y. Kalinci, A. Hepbasli, I. Dincer, Biomass-based hydrogen production: a review and analysis, *Int. J. Hydrogen Energ.*, 34 (21) (2009) 8799-8817.
- [3] R. Saidur, E.A. Abdelaziz, A. Demirbas, M.S. Hossain, S. Mekhilef, A review on biomass as a fuel for boilers, *Renew. Sust. Energ. Rev.*, 15 (5) (2011) 2262-2289.
- [4] B. Moghtaderi, Review of the recent chemical looping process developments for novel energy and fuel applications, *Energ. Fuel.*, 26 (1) (2012) 15-40.
- [5] J. Adanez, A. Abad, T. Mendiara, P. Gayan, L.F. de Diego, F. Garcia-Labiano, Chemical looping combustion of solid fuels, *Prog. Energ. Combust.*, 65 (2018) 6-66.
- [6] J. Adanez, A. Abad, F. Garcia-Labiano, P. Gayan, L.F. de Diego, Progress in chemical-looping combustion and reforming technologies, *Prog. Energ. Combust.*, 38 (2) (2012) 215-282.
- [7] Q.J. Guo, X.D. Hu, Y.Z. Liu, W.H. Jia, M.M. Yang, M. Wu, H.J. Tian, H.J. Ryu, Coal chemical-looping gasification of Ca-based oxygen carriers decorated by CaO, *Powder Technol.*, 275 (2015) 60-68.
- [8] J. Strohle, M. Orth, B. Eppele, Design and operation of a 1 MW_{th} chemical looping plant, *Appl. Energ.*, 113 (2014) 1490-1495.
- [9] T.B. Vilches, H. Thunman, Experimental investigation of volatiles-bed contact in a 2-4 MW_{th} bubbling bed reactor of a dual fluidized bed gasifier, *Energ. Fuel.*, 29 (10) (2015) 6456-6464.
- [10] J.S. Zhang, Simulation study on 10MW_{th} coal based chemical looping gasification process, *M.Eng. Thesis, QUST.*, China, 2012.
- [11] S.G. Nadgouda, M.Q. Guo, A. Tong, L.S. Fan, High purity syngas and hydrogen coproduction using copper-iron oxygen carriers in chemical looping reforming process, *Appl. Energ.*, 235 (2019) 1415-1426.
- [12] K. Wang, Q.B. Yu, Q. Qin, W.J. Duan, Thermodynamic modeling of the combined CLG-CLHG system for syngas and hydrogen generation, *Environ. Prog. Sustain.*, 37 (3) (2018) 1132-1139.
- [13] H.J. Ge, H.F. Zhang, W.J. Guo, T. Song, L.H. Shen, System simulation and experimental verification: biomass-based integrated gasification combined cycle (BIGCC) coupling with chemical looping gasification (CLG) for power generation, *Fuel*, 241 (2019) 118-128.
- [14] A.T. Wijayanta, M. Aziz, Ammonia production from algae via integrated hydrothermal gasification, chemical looping, N₂ production, and NH₃ synthesis, *Energy*, 174 (2019) 331-338.
- [15] M. Aziz, I.N. Zaini, T. Oda, A. Morihara, T. Kashiwagi, Energy conservative brown coal conversion to hydrogen and power based on enhanced process integration: Integrated drying, coal direct chemical looping, combined cycle and hydrogenation, *Int. J. Hydrogen Energ.*, 42 (5) (2017) 2904-2913.
- [16] Z. Yu, Y. Yang, S. Yang, Q. Zhang, J. Zhao, Y. Fang, X.G. Hao, G.Q. Guan, Iron-based oxygen

- carriers in chemical looping conversions: a review, *Carbon Resources Conversion*, 2 (1) (2019) 23-34.
- [17] F.X. Li, H.R. Kim, D. Sridhar, F. Wang, L. Zeng, J. Chen, L.S. Fan, Syngas chemical looping gasification process: oxygen carrier particle selection and performance, *Energ. Fuel*, 23 (8) (2009) 4182-4189.
- [18] T. Mendiara, L.F. de Diego, F. García-Labiano, P. Gayan, A. Abad, J. Adanez, On the use of a highly reactive iron ore in chemical looping combustion of different coals, *Fuel*, 126 (2014) 239-49.
- [19] A. Petros, P. R. Davidson, G. Skodras, 6th International Conference on Clean Coal Technologies CCT2013, *Appl. Therm. Eng.*, 74 (2015) 1-210.
- [20] R. Perez-Vega, I. Adanez-Rubio, P. Gayan, M.T. Izquierdo, A. Abad, F. García-Labiano, L.F. de Diego, J. Adanez, Sulphur, nitrogen and mercury emissions from coal combustion with CO₂ capture in chemical looping with oxygen uncoupling (CLOU), *Int. J. Greenh. Gas. Con.*, 46 (2016) 28-38.
- [21] M. Abian, A. Abad, M.T. Izquierdo, P. Gayan, L.F. de Diego, F. García-Labiano, J. Adanez, Titanium substituted manganese-ferrite as an oxygen carrier with permanent magnetic properties for chemical looping combustion of solid fuels, *Fuel*, 195 (2017) 38-48.
- [22] J. Fan, L. Zhu, H. Hong, Q. Jiang, H. Jin, A thermodynamic and environmental performance of in-situ gasification of chemical looping combustion for power generation using ilmenite with different coals and comparison with other coal-driven power technologies for CO₂ capture, *Energy*, 119 (2017) 1171-1180.
- [23] A. Edrisi, Z. Mansoori, B. Dabir, A. Shahnazari, Hydrogen, nitrogen and carbon dioxide production through chemical looping using iron-based oxygen carrier-a Green plant for H₂ and N₂ production, *Int. J. Hydrogen Energ.*, 39 (20) (2014) 10380-10391.
- [24] Y. L. Kuo, W.C. Huang, W. M. Hsu, Y. H. Tseng, Y. Ku, Use of spinel nickel aluminium ferrite as self-supported oxygen carrier for chemical looping hydrogen generation process, *Aerosol Air Qual. Res.*, 15 (7) (2015) 2700-2708.
- [25] T. Liu, S. Hu, Z. Yu, J. Huang, J. Li, Z. Wang, Y. Fang, Research of coal-direct chemical looping hydrogen generation with iron-based oxygen carrier modified by potassium, *Int. J. Hydrogen Energ.*, 42 (16) (2017) 11038-11046.
- [26] A. Tong, D. Sridhar, Z.C. Sun, H.R. Kim, L. Zeng, F. Wang, D.W. Wang, M.V. Kathe, S.W. Luo, Y.H. Sun, L.S. Fan, Continuous high purity hydrogen generation from a syngas chemical looping 25kW(th) sub-pilot unit with 100% carbon capture, *Fuel*, 103 (2013) 495-505.
- [27] L.L. Wang, L.H. Shen, W.D. Liu, S.X. Jiang, Chemical looping hydrogen generation using synthesized hematite-based oxygen carrier comodified by potassium and copper, *Energ. Fuel*, 31(8) (2017) 8423-8433.
- [28] X. Zhang, H. Jin. Thermodynamic analysis of chemical-looping hydrogen generation, *Appl. Energ.*, 112 (2013) 800-807.
- [29] M.N. Khan, T. Shamim, Investigation of hydrogen generation in a three reactor chemical looping reforming process, *Appl. Energ.*, 162 (2016) 1186-1194.
- [30] H.Z. Liu, Synthetic ammonia industry: past, present and future-review, enlightenment and

challenges of the 100th anniversary of the establishment of synthetic ammonia industry, *Chem. Ind. & Eng. Pro.(China)*, 32 (09) (2013) 1995-2005.

[31] D. Xiang, Y. Zhou, Concept design and techno-economic performance of hydrogen and ammonia co-generation by coke-oven gas-pressure swing adsorption integrated with chemical looping hydrogen process, *Appl. Energ.*, 229 (2018)1024-1034.

[32] M. Ishida, H. Jin, A novel chemical-looping combustor without NO_x formation, *Ind. Eng. Chem. Res.*, 35 (7) (1996) 2469-2472.

[33] A. Edrisi, Z. Mansoori, B. Dabir, Using three chemical looping reactors in ammonia production process - A novel plant configuration for a green production, *Int. J. Hydrogen Energ.*, 39 (16) (2014) 8271-8282.

[34] A-M. Cormos, C-C. Cormos, Investigation of hydrogen and power cogeneration based on direct coal chemical looping systems, *Int. J. Hydrogen Energ.*, 39 (5) (2014) 2067-2077.

[35] Y.D. He, L. Zhu, L.L. Li, L. Sun, Zero-energy penalty carbon capture and utilization for liquid fuel and power cogeneration with chemical looping combustion, *J. Clean. Prod.*, 235 (2019) 34-43.

[36] D. Xiang, W.Q. Huang, M.D. Cai, Y. Cao, P. Li, R.W. Shu, Process modeling, simulation, and technical analysis of coke-oven gas solid oxide fuel cell integrated with anode off-gas recirculation and CLC for power generation, *Energ. Convers. Manage.*, 190 (2019) 34-41.

[37] C.D. Demirhan, W.W. Tso, J.B. Powell, E.N. Pistikopoulos, Sustainable ammonia production through process synthesis and global optimization, *AIChE J.*, 65(7) (2019) e16498.

[38] A. Darmawan, M.W. Ajiwibowo, K. Tokimatsu, M. Aziz, Efficient co-production of power and ammonia from black liquor, *Int. J. Hydrogen Energ.*, DOI: 10.1016/j.ijhydene. 2020.02.196.

[39] C.H. Liu, Analysis of coal market supply and demand in the first half of 2019 and prediction of trend in the second half of 2019, *Journal of Commercial economics*, 2019, 21: 185-186.

[40] A. Cuadrat, A. Abad, J. Adanez, L.F. de Diego, F. García-Labiano, P. Gayan, Behavior of ilmenite as oxygen carrier in chemical-looping combustion, *Fuel Process.Technol.*, 94 (1) (2012) 101-112.

[41] L. Zhu, Y.D. He, L.L. Li, P.B. Wu, Tech-economic assessment of second-generation CCS: chemical looping combustion, *Energy*, 144 (2018) 915-927.

[42] A.E. Farooqui, A. Bose, D. Ferrero, J. Llorca, M. Santarelli, Simulation of two-step redox recycling of non-stoichiometric ceria with thermochemical dissociation of CO₂/H₂O in moving bed reactors-Part II:Techno-economic analysis and integration with 100MW oxyfuel power plant with carbon capture, *Chem. Eng. Sci.*, 205 (2019) 358-373.

[43] R.C. Baliban, J.A. Elia, C.A. Floudas, Toward novel hybrid biomass, coal, and natural gas processes for satisfying current transportation fuel demands, 1: process alternatives, gasification modeling, process simulation, and economic analysis, *Ind. Eng. Chem. Res.*, 49 (16) (2010) 7343-7370.

[44] P. Jiang, A.S. Berrouk, S. Dara, Biomass gasification integrated with chemical looping system for hydrogen and power coproduction process-thermodynamic and techno-economic assessment, *Chem. Eng. Technol.*, 42 (5) (2019) 1153-1168.

- [45] A.K. Olaleye, M.H. Wang, Techno-economic analysis of chemical looping combustion with humid air turbine power cycle, *Fuel*, 124 (2014) 221-231.
- [46] S. Roussanaly, M. Vitvarova, R. Anantharaman, D. Berstad, B. Hagen, J. Jakobsen, V. Novotny, G. Skaugen, Techno-economic comparison of three technologies for pre-combustion CO₂ capture from a lignite-fired IGCC, *Front. Chem. Sci. Eng.*, 14 (3) (2020) 436–452.
- [47] N. Nakaten, T. Kempka, Techno-economic comparison of onshore and offshore underground coal gasification end-product competitiveness, *Energies*, 12 (17) (2019).

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: