

## PAPER

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2025, 9, 6761Process modelling and thermodynamic analysis of  
hydrogen production through chemical looping  
ammonia crackingAnantha Krishnan Vinayak Soman, Siqi Wang,  \* Ziqi Shen  and Mingming Zhu

In this study, a novel chemical looping ammonia cracking (CLCr) process was designed for efficient hydrogen production. A closed-loop, three-reactor chemical looping system using iron oxide as the oxygen carrier was modelled in Aspen Plus. A parametric study was carried out to evaluate the effect of key parameters, including the air reactor outlet temperature, fuel reactor outlet temperature, ammonia to oxygen carrier ratio, and the steam reactor pressure. The optimal operating conditions were then identified, under which a hydrogen yield of 69.4% with 99.99% purity can be achieved with an overall energy efficiency of 79.6%. An energy balance analysis was also carried out to confirm that the process is autothermal, and the overall exergy efficiency of the process was 70.4%. These findings highlight the novel CLCr process as an energy-efficient alternative to conventional ammonia catalytic cracking for hydrogen production.

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## Introduction

Hydrogen has gained increasing attention as a clean energy vector in the transition to a net-zero future. Different sustainable hydrogen production pathways are being developed to complement conventional fossil fuel-based processes, such as water electrolysis and biomass gasification.<sup>1</sup> However, a common challenge across all pathways is the need for safe, efficient, and scalable storage and distribution of hydrogen. As a mature commodity, ammonia has emerged as a promising hydrogen carrier, due to its high hydrogen content (17.8 wt%), easy storage, and well-established global infrastructure network for production, distribution, and storage, developed over a century of large-scale use in the fertiliser industry.<sup>2–4</sup>

As a hydrogen carrier, ammonia needs to be converted back to hydrogen at the end-use point. Currently, the predominant pathway to convert ammonia into hydrogen is through thermocatalytic ammonia cracking. One of the limitations of this process is that the reaction is highly endothermic (46 kJ mol<sup>−1</sup> NH<sub>3</sub>) with additional energy required for liquid ammonia vaporisation (23.4 kJ mol<sup>−1</sup>) and preheating (liquid ammonia heat capacity of 50 J mol<sup>−1</sup> K<sup>−1</sup>).<sup>5</sup> Moreover, of all the catalysts tested for the reaction, Ru-based catalysts remain the performance benchmark, limiting the scalability of the process due to their cost. Although non-noble metal-based and bimetallic alternatives have been studied, the reaction temperature required for these catalysts to reach a desirable reaction rate remains high.<sup>6,7</sup> Aside from the kinetics and catalyst

limitations, an inherent challenge of the process is the extensive purification process required for the reactor off-gas, which contains a 1 : 3 molar ratio mixture of N<sub>2</sub> to H<sub>2</sub> with unreacted NH<sub>3</sub>, to produce a high-purity hydrogen stream.

The Chemical Looping (CL) technology provides a suitable option to address the challenges faced by conventional thermocatalytic ammonia cracking. CL has been extensively studied for hydrogen production from methane and other hydrocarbon fuels.<sup>8–12</sup> In addition, the CL process can be integrated with renewable energy and bio-feedstocks to improve energy efficiency and reduce carbon emission. For example, solar-assisted chemical looping systems have been proposed to combine redox cycles with concentrated solar energy, significantly improving hydrogen yield while reducing emissions.<sup>13</sup> CO<sub>2</sub>-rich waste gases, such as landfill gases, have also been explored as alternative feedstocks for syngas production, offering a sustainable route for both hydrogen production and CO<sub>2</sub> utilisation.<sup>14</sup>

A typical three-reactor CL process involves three main steps: (1) the reactions between the fuel and the oxygen carrier (metal oxides) to produce carbon dioxide in the Fuel Reactor (FR); (2) the reactions between the reduced oxygen carrier and steam to produce hydrogen in the Steam Reactor (SR); (3) the reaction between the oxygen carrier and air to regenerate the oxygen carrier and produce an oxygen-depleted N<sub>2</sub> stream in the Air Reactor (AR).

In this study, a closed-looped three-reactor CL process for ammonia cracking is conceptualised, named as Chemical Looping Ammonia Cracking (CLCr), where iron oxide is used as the oxygen carrier to crack ammonia and produce ultra-high purity hydrogen. Iron oxide was selected as the oxygen carrier

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(OC) due to its abundance, thermal stability, and low cost.<sup>15</sup> In the chemical looping reforming (CLR) process, iron oxides also showed good reactivity, high oxygen adsorption capacity, and high resistance against sintering.<sup>16,17</sup> Recent studies on iron ore direct reduction using ammonia suggest that it is feasible to use iron oxides as an oxygen carrier for ammonia reduction.<sup>18,19</sup> Furthermore, experimental thermogravimetric analyses reported by Ma *et al.* showed that  $\text{Fe}_2\text{O}_3$  can be fully reduced under  $\text{NH}_3$  at 700 °C without the formation of  $\text{NO}_x$ ,<sup>20</sup> confirming its reducibility under ammonia-rich environment. In addition, metallic Fe – formed upon complete reduction of iron oxides – has been demonstrated to be active for ammonia decomposition.<sup>21</sup> These experimental findings are consistent with the reaction pathways considered in this work, providing confidence in the feasibility of the proposed process. This work aims to design a CLCr process *via* Aspen Plus modelling and evaluate the effect of key process parameters on the performance of the system through a parametric analysis. Finally, a process was developed using the optimal operation conditions identified in the parametric analysis and the thermodynamic analysis was carried out on the optimised process.

## Methodology

### Process description

The novel CLCr process proposed in this work consists of three main reactors, the fuel reactor (FR), the steam reactor (SR), and the air reactor (AR). A block diagram of the process is shown in Fig. 1. The reactions which take place in the three reactors are summarised in Table 1.

### Aspen Plus model setup

The steady-state modelling of the proposed CLCr process was carried out using the Aspen Plus v12.2 software. The components used in the model are summarised in Table 2.  $\text{N}_2\text{O}$  and  $\text{NO}$  were defined as components to estimate  $\text{NO}_x$  formation in the FR.  $\text{Fe}_4\text{N}$  was included as a component, as its formation from the reaction between  $\text{Fe}^0$  and ammonia hinders the reoxidation of  $\text{Fe}^0$ .<sup>18</sup> Considering the potential sintering and attrition of the OC material under real-life conditions,  $\text{Al}_2\text{O}_3$  was

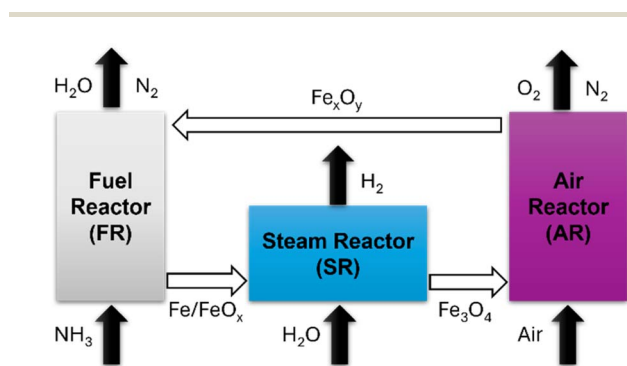


Fig. 1 Block diagram of the proposed ammonia CLCr process.

Table 2 List of components used in the Aspen Plus model

| Name                        | Type         | Component name   | Databank         |
|-----------------------------|--------------|------------------|------------------|
| $\text{Fe}_2\text{O}_3$     | Solid        | Hematite         | APV121.PU        |
| $\text{Fe}_3\text{O}_4$     | Solid        | Magnetite        | APV121.SOLIDS    |
| $\text{Fe}_{0.947}\text{O}$ | Solid        | Wustite          | APV121.INORGANIC |
| Fe                          | Solid        | Iron             | APV121.PURE39    |
| $\text{Al}_2\text{O}_3$     | Solid        | Alumina          | APV121.PURE39    |
| $\text{Fe}_4\text{N}$       | Solid        | Iron nitride     | APV121.INORGANIC |
| $\text{NH}_3$               | Conventional | Ammonia          | APV121.PURE39    |
| $\text{N}_2$                | Conventional | Nitrogen         | APV121.PURE39    |
| $\text{H}_2$                | Conventional | Hydrogen         | APV121.PURE39    |
| $\text{O}_2$                | Conventional | Oxygen           | APV121.PURE39    |
| $\text{H}_2\text{O}$        | Conventional | Water            | APV121.PURE39    |
| $\text{NO}_2$               | Conventional | Nitrogen dioxide | APV121.PURE39    |
| $\text{NO}$                 | Conventional | Nitric oxide     | APV121.PURE39    |
| $\text{N}_2\text{O}$        | Conventional | Nitrous oxide    | APV121.PURE39    |

Table 1 List of reactions which take place in the CLCr process

|               |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
|---------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Fuel reactor  | $\text{NH}_3 \xrightarrow{\text{Fe/Fe}_3\text{O}_4} 0.5\text{N}_2 + 1.5\text{H}_2, \Delta H_{298}^\circ = +45.94\text{ kJ mol}^{-1}$ (1)<br>$\text{Fe}_2\text{O}_3 + 0.222\text{NH}_3 \rightarrow 0.667\text{Fe}_3\text{O}_4 + 0.111\text{N}_2 + 0.333\text{H}_2\text{O}, \Delta H_{298}^\circ = +7.28\text{ kJ mol}^{-1}$ (2)<br>$\text{Fe}_3\text{O}_4 + 0.554\text{NH}_3 \rightarrow 3.168\text{Fe}_{0.947}\text{O} + 0.277\text{N}_2 + 0.832\text{H}_2\text{O}, \Delta H_{298}^\circ = +83.30\text{ kJ mol}^{-1}$ (3)<br>$\text{Fe}_{0.947}\text{O} + 0.667\text{NH}_3 \rightarrow 0.947\text{Fe} + 0.333\text{N}_2 + \text{H}_2\text{O}, \Delta H_{298}^\circ = +76.15\text{ kJ mol}^{-1}$ (4)<br>$\text{Fe}_2\text{O}_3 + 0.333\text{H}_2 \rightarrow 0.667\text{Fe}_3\text{O}_4 + 0.333\text{H}_2\text{O}, \Delta H_{298}^\circ = -2.66\text{ kJ mol}^{-1}$ (5)<br>$\text{Fe}_3\text{O}_4 + 0.832\text{H}_2 \rightarrow 3.168\text{Fe}_{0.947}\text{O} + 0.832\text{H}_2\text{O}, \Delta H_{298}^\circ = +57.86\text{ kJ mol}^{-1}$ (6)<br>$\text{Fe}_{0.947}\text{O} + \text{H}_2 \rightarrow 0.947\text{Fe} + \text{H}_2\text{O}, \Delta H_{298}^\circ = +30.21\text{ kJ mol}^{-1}$ (7)<br>$\text{Fe}_3\text{O}_4 + 0.788\text{Fe} \rightarrow 4\text{Fe}_{0.947}\text{O} + \text{H}_2\text{O}, \Delta H_{298}^\circ = +32.73\text{ kJ mol}^{-1}$ (8)<br>$\text{Fe}_{0.947}\text{O} \rightarrow 0.25\text{Fe}_3\text{O}_4 + 0.197\text{Fe}, \Delta H_{298}^\circ = -8.18\text{ kJ mol}^{-1}$ (9) |
| Steam reactor | $\text{Fe} + 1.056\text{H}_2\text{O}(\text{g}) \rightarrow \text{Fe}_{0.947}\text{O} + 1.056\text{H}_2, \Delta H_{298}^\circ = -31.90\text{ kJ mol}^{-1}$ (10)<br>$\text{Fe} + 1.056\text{H}_2\text{O}(\text{l}) \rightarrow \text{Fe}_{0.947}\text{O} + 1.056\text{H}_2, \Delta H_{298}^\circ = +14.56\text{ kJ mol}^{-1}$ (11)<br>$\text{Fe}_{0.947}\text{O} + 0.263\text{H}_2\text{O}(\text{g}) \rightarrow 0.316\text{Fe}_3\text{O}_4 + 0.263\text{H}_2, \Delta H_{298}^\circ = -18.56\text{ kJ mol}^{-1}$ (12)<br>$\text{Fe}_{0.947}\text{O} + 0.263\text{H}_2\text{O}(\text{l}) \rightarrow 0.316\text{Fe}_3\text{O}_4 + 0.263\text{H}_2, \Delta H_{298}^\circ = -6.98\text{ kJ mol}^{-1}$ (13)<br>$\text{Fe} + 1.333\text{H}_2\text{O}(\text{g}) \rightarrow 0.333\text{Fe}_3\text{O}_4 + 1.333\text{H}_2, \Delta H_{298}^\circ = -48.26\text{ kJ mol}^{-1}$ (14)<br>$\text{Fe} + 1.333\text{H}_2\text{O}(\text{l}) \rightarrow 0.333\text{Fe}_3\text{O}_4 + 1.333\text{H}_2, \Delta H_{298}^\circ = +10.26\text{ kJ mol}^{-1}$ (15)                                                                                                                                                                                                                                                                                                                                                                                                                                                               |
| Air reactor   | $\text{Fe}_{0.947}\text{O} + 0.211\text{O}_2 \rightarrow 0.474\text{Fe}_2\text{O}_3, \Delta H_{298}^\circ = -119.00\text{ kJ mol}^{-1}$ (16)<br>$\text{Fe}_3\text{O}_4 + 0.25\text{O}_2 \rightarrow 1.5\text{Fe}_2\text{O}_3, \Delta H_{298}^\circ = -117.36\text{ kJ mol}^{-1}$ (17)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |



Table 3 Properties used for the main blocks and model assumptions

| Subjects                                                | Selection                                       | References        |
|---------------------------------------------------------|-------------------------------------------------|-------------------|
| <b>Properties</b>                                       |                                                 |                   |
| Property method                                         | PR-BM                                           | 28–31             |
| Steam class                                             | MIXCISLD                                        | 32                |
| <b>Unit operation blocks</b>                            |                                                 |                   |
| Reactors                                                | RGibbs                                          | 30, 31, 33 and 34 |
| Heat exchangers                                         | HeatX                                           | 35                |
| Heaters                                                 | Heater                                          | 28                |
| Pressure changers                                       | Compr, valve                                    | 28                |
| Separators                                              | Flash2                                          | 28                |
| <b>Assumptions</b>                                      |                                                 |                   |
| Ambient conditions                                      | 1 atm, 25 °C                                    | 34                |
| Pressure drops                                          | Zero                                            | 30, 33 and 36–38  |
| Air                                                     | 79 mol% N <sub>2</sub> , 21 mol% O <sub>2</sub> | 28, 34 and 39     |
| Minimum approach temperature (MAT) of heat exchangers   | 10 °C                                           | 34, 40 and 41     |
| Minimum approach temperature (MAT) of steam generator   | 10 °C                                           | 34, 40 and 41     |
| Minimum approach temperature (MAT) of ammonia vaporiser | 3 °C                                            | 41                |
| Isentropic efficiency-compressor                        | 89%                                             | 34 and 42         |
| Mechanical efficiency-compressor                        | 97%                                             | 34 and 40         |
| Pump efficiency                                         | 90%                                             | 34 and 40         |
| Isentropic efficiency-turbine                           | 93%                                             | 34 and 42         |
| Mechanical efficiency-turbine                           | 96.6%                                           | 40 and 42         |
| Generator efficiency                                    | 99%                                             | 43                |
| Reactors of FR, AR and SR                               | Adiabatic, Gibbs free energy minimisation       | 40                |
| Reactor operating pressure                              | 1 atm                                           | 29 and 38         |
| Feed ammonia stream conditions                          | 10 bar, 25 °C                                   | 44                |
| Cooling utility (air/water)                             | 25 °C                                           |                   |

included as a heat carrier with Fe<sub>2</sub>O<sub>3</sub> for its good specific heat capacity.<sup>22,23</sup> Al<sub>2</sub>O<sub>3</sub> was regarded as an inert material, thus the FeAl<sub>2</sub>O<sub>4</sub>, formed by the reaction between Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>, was not defined as a component.<sup>24–26</sup> RGibbs blocks were used to simulate all reactors, accounting for all possible reaction pathways within the defined components and neglecting mass transfer limitations.<sup>26</sup> The counter-current moving-bed reactor was selected for the FR, which was simulated by 7 RGibbs blocks. The SR and AR were simulated by one RGibbs block each. The counter-current moving-bed reactors, based on the experimental and modelling study of a 25 kW<sub>th</sub> syngas CL system using iron-based OCS, achieved high syngas conversion and continuous production of high-purity hydrogen.<sup>27</sup> The system was simulated under a pressure of 1 bar, and its performance was assessed across an AR outlet temperature (*T*<sub>Ao</sub>) in the range of 880 – 1150 °C. The properties of the main blocks and the assumptions made for the model development are summarised in Table 3.

### System performance evaluation

To evaluate the performance of the process, 8 metrics were used with their definitions and equations summarised in Table 4.

The thermodynamic analysis also includes heat balance, which can be evaluated using the following method. Under autothermal conditions, the net heat of oxidation of the steam

in the SR ( $\Delta H_{\text{SR}}^0$ ) plus the heat of combustion of hydrogen should be equal to the heat of oxidation of the equivalent OC in AR ( $\Delta H_{\text{AR}}^0$ ), defined as below:

$$\Delta H_{\text{Red}}^R + \Delta H_{\text{CombH}_2}^0 + \Delta H_{\text{AR}}^0 + \Delta H_{\text{SR}}^0 = \Delta H_{\text{CombNH}_3}^0 \quad (29)$$

In the meantime:

$$\Delta H_{\text{Red}}^R = \left| \Delta H_{\text{CombNH}_3\text{-fuel}}^0 \right| + \left| \Delta H_{\text{SR}}^0 \right| \quad (30)$$

where  $\Delta H_{\text{CombNH}_3\text{-fuel}}^0$  is the fuel fraction of ammonia in the ammonia CLCr process. Fig. 2 shows the energy inputs and outputs in the CLCr process. For the calculation of the heat consumed in FR ( $Q_{\text{heat-sink}}$ ), the following were considered: the heat from input oxides ( $Q_i$ ) and gas ( $Q_{\text{NH}_3}$ ), the heat remaining in the output reduced oxides ( $Q_o$ ), and direct loss ( $Q_v$ ).

The heat input can be calculated with eqn (31) and (32):

$$Q_i = m_i C_{\text{pi}} (T_{\text{Ao}} - 25) \quad (31)$$

$$Q_{\text{NH}_3} = M_{\text{NH}_3} C_{\text{p-NH}_3} (T_{\text{NH}_3} - 25) \quad (32)$$

The heat remaining in the output reduced oxides can be calculated with eqn (33):

$$Q_o = m_o C_{\text{po}} (T_{\text{Fo}} - 25) \quad (33)$$



Table 4 8 Performance evaluation metrics in this study

| Metrics                                                      | Definitions                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |
|--------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Hydrogen yield                                               | $Y_{H_2}(\%) = \frac{M_{H_2}}{M_{NH_3} \times 0.178} \times 100 \quad (18)$ <p>In which <math>M_{H_2}</math> and <math>M_{NH_3}</math> were the mass flow rates of hydrogen and ammonia in <math>kg\ h^{-1}</math>, respectively</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |
| Overall energy efficiency based on lower heating value (LHV) | $\eta_{OEE} = \frac{LHV_{H_2} M_{H_2}}{LHV_{NH_3} M_{NH_3} + \frac{W_{comp}}{\eta_{heat\ to\ power}} + \frac{Q_{process}}{\eta_{comp}}} \quad (19)$ <p>In which <math>LHV_{H_2}</math>, <math>LHV_{NH_3}</math> were the lower heating value of hydrogen and ammonia in <math>kJ\ kg^{-1}</math>, respectively. <math>W_{comp}</math> was the power requirement for compression in kWh. <math>Q_{process}</math> was the external heat requirement of the process. The conversion efficiency from heat to power <math>\eta_{heat\ to\ power} = 0.123\ kWh\ MJ^{-1}</math>. The efficiency <math>\eta_{comp} = 0.89</math></p>                                                                                                                                                                                   |
| Cold gas efficiency based on higher heating value (HHV)      | $\eta_{CGE} = \frac{HHV_{H_2} M_{H_2}}{HHV_{NH_3} M_{NH_3}} \quad (20)$ <p>In which <math>HHV_{H_2}</math>, <math>HHV_{NH_3}</math> were the higher heating value of hydrogen and ammonia in <math>kJ\ kg^{-1}</math>, respectively</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |
| Extent of reduction                                          | $E_{red} = \frac{M_{Fe_2O_3} - M_{RedOx}}{M_{Fe_2O_3} - M_{Fe}} \quad (21)$ <p>In which <math>M_{Fe_2O_3}</math>, <math>M_{RedOx}</math> and <math>M_{Fe}</math> were the mass flow rates of iron oxide (<math>Fe_2O_3</math>), reduced oxides of iron, and fully reduced iron oxides (Fe), respectively</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |
| Theoretical maximum hydrogen generation                      | $m_{H_2,max} \left( \frac{kg}{h} \right) = 2 \times MW_{H_2} \times (F_{O_2} - F_{O_2}^{Fe_3O_4}) \quad (22)$ $F_{O_2}^{Fe_3O_4} = \frac{M_{Fe_2O_3} - 0.667 \times \left( \frac{M_{Fe_2O_3}}{MW_{Fe_2O_3}} \right) \times MW_{Fe_3O_4}}{MW_{O_2}} \quad (23)$ <p>In which <math>M_{Fe_2O_3}</math> was the mass flow rate of <math>Fe_2O_3</math> in <math>kg\ h^{-1}</math>. <math>MW_{O_2}</math>, <math>MW_{H_2}</math>, <math>MW_{Fe_2O_3}</math>, <math>MW_{Fe_3O_4}</math> were the molar mass of <math>O_2</math>, <math>H_2</math>, <math>Fe_2O_3</math> and <math>Fe_3O_4</math> in <math>kg\ kmol^{-1}</math>. <math>F_{O_2}</math> and <math>F_{O_2}^{Fe_3O_4}</math> were the molar flow rates of <math>O_2</math> and the <math>O_2</math> consumed by the reaction with <math>Fe_3O_4</math></p> |
| Theoretical maximum hydrogen yield                           | $Y_{Theo} = \frac{m_{H_2,max}}{0.178 \times M_{NH_3}} \quad (24)$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |
| Fraction of fuel energy loss                                 | $F_L = \frac{Q_{Loss}}{M_{NH_3} HHV_{NH_3}} \times 100 \quad (25)$ <p>In which <math>Q_{Loss}</math> was the total process heat loss in <math>kJ\ h^{-1}</math></p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |
| Exergy efficiency of the process                             | $\eta_e = \frac{Ex_{H_2}}{Ex_{feed} + \frac{W_{comp}}{\eta_{heat\ to\ power}}} \quad (26)$ <p>In which <math>Ex_{H_2}</math> and <math>Ex_{feed}</math> were the total exergy of hydrogen and the feed gas, respectively. Two types of exergies were considered, the chemical and the physical exergy. The total exergy was defined as the sum of the two types of exergies</p> $Ex_{total} = Ex_{chemical} + Ex_{physical} \quad (27)$ <p>The chemical exergy of the gas mixture can be calculated using the equation below</p> $Ex_{chemical} = N_i \left[ \sum_{i=1}^n Ex_i + RT_0 x_i \sum_{i=1}^n x_i \ln x_i \right] \quad (28)$ <p>In which <math>N_i</math> and <math>x_i</math> were the number of moles and the mole fraction of the component <math>i</math> in the gas mixture, respectively</p>    |

The heat loss in FR vent ( $Q_v$ ) can be collected from the model.

The net heat consumed in FR can be then calculated using eqn (34):

$$Q_{heat-sink} = Q_i + Q_{NH_3} - Q_o - Q_v \quad (34)$$

For the calculation of the net heat generated in heat source ( $Q_{heat-source}$ ), the following were considered: the heat from the fuel-fraction of ammonia ( $\Delta H_{CombNH_3-fuel}^0$ ), the heat of oxidation of the steam in the SR ( $\Delta H_{SR}^0$ ). The heat loss from the AR and SR vent were considered as 0 as the AR gas vent was cooled to 25 °C and the SR gas vent was cooled to be below zero in the model.

The fuel-fraction of the mass flow of ammonia ( $M_{NH_3-fuel}$ ) can be calculated using eqn (35):

$$M_{NH_3-fuel} = M_{NH_3} - \frac{M_{H_2}}{0.178} \quad (35)$$

The heat of oxidation of the steam in the SR ( $\Delta H_{SR}^0$ ) can be collected from the model.

$$\Delta H_{CombNH_3-fuel}^0 = HHV \cdot M_{NH_3-fuel} \quad (36)$$

The net heat generated in the SR and AR can then be calculated using (eqn (37)):

$$Q_{heat-source} = \Delta H_{CombNH_3-fuel}^0 + \Delta H_{SR}^0 \quad (37)$$



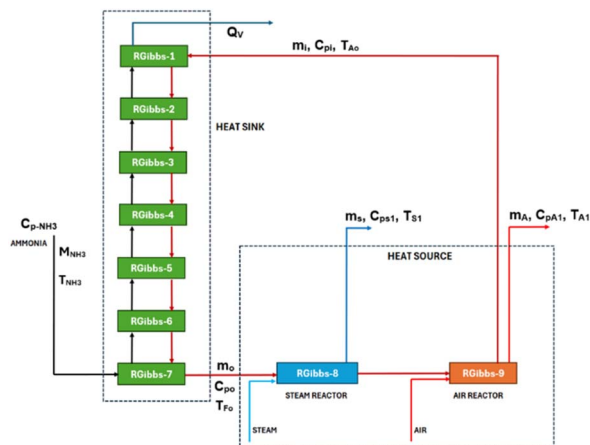


Fig. 2 Schematic diagram of the heat flow of the CLCr process.  $Q_v$ : the vent heat loss from the FR in  $\text{MJ h}^{-1}$ .  $M_{\text{NH}_3}$ : the total flow rate of ammonia in  $\text{kg h}^{-1}$ .  $m_k$  ( $k = s, A, i, o$ ): the mass flow rates of the SR vent, AR vent, FR inlet solid, and FR solid in  $\text{kg h}^{-1}$ .  $C_{pk}$  ( $k = s1, A1, \text{NH}_3, o, i$ ): the mass-specific heat capacities of the SR vent, AR vent, ammonia, FR outlet solid, and FR inlet solid in  $\text{kJ kg}^{-1} \text{ } ^\circ\text{C}^{-1}$ .  $T_k$  ( $k = Ao, S1, A1, \text{NH}_3, Fo$ ): temperatures of the FR inlet, SR outlet gas after cooling, AR vent after heat recovery, ammonia inlet, and the FR outlet.

## Results and discussion

### Parametric study

Based on the block program (Fig. 1), an Aspen Plus model was developed, and an example of the schematic diagram is presented in Fig. 3. Four key parameters were chosen to evaluate their effects on the model performance: the AR outlet temperature ( $T_{Ao}$ ), the FR outlet temperature ( $T_{Fo}$ ), the ammonia to oxygen carrier ratio ( $R_{\text{NH}_3/\text{OC}}$ , based on mass flow rates), and the SR pressure.

### Effect of the AR outlet temperature ( $T_{Ao}$ )

In this section, the effect of  $T_{Ao}$  within the range of 880 – 1080  $^\circ\text{C}$  was evaluated, and the results are presented in Fig. 4. Temperatures below 880  $^\circ\text{C}$  were excluded to ensure high levels of OC reduction and to prevent  $\text{Fe}_{0.947}\text{O}$  disproportionation in the FR. In this study, the solid at the AR outlet remained fully oxidised at stoichiometric air conditions with a circulation rate of 20 000  $\text{kg h}^{-1}$ . The  $\text{Fe}_2\text{O}_3$  mass fraction was 0.758, with the remainder being the heat carrier,  $\text{Al}_2\text{O}_3$ . The flow rate of ammonia was fixed at around 1400  $\text{kg h}^{-1}$ , simulating the scale

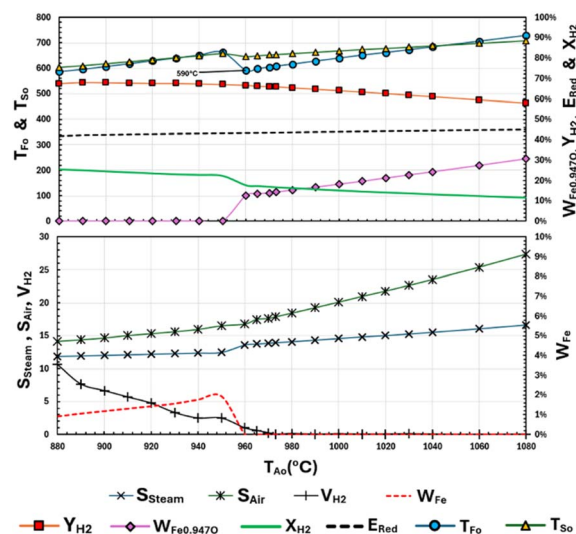


Fig. 4 Effect of  $T_{Ao}$  on hydrogen yield ( $Y_{\text{H}_2}$ ), extent of reduction ( $E_{\text{Red}}$ ), mass fractions of  $\text{Fe}_{0.947}\text{O}$  and Fe slip to AR ( $W_{\text{Fe}_{0.947}\text{O}}$ ,  $W_{\text{Fe}}$ ), specific steam consumption ( $S_{\text{steam}}$ ), specific air consumption ( $S_{\text{air}}$ ), mass fractions of  $\text{H}_2$  in the SR gas outlet ( $X_{\text{H}_2}$ ) and  $\text{H}_2$  in the FR vent ( $Y_{\text{H}_2}$ ), SR outlet temperature ( $T_{So}$ ), and FR outlet temperature ( $T_{Fo}$ ).

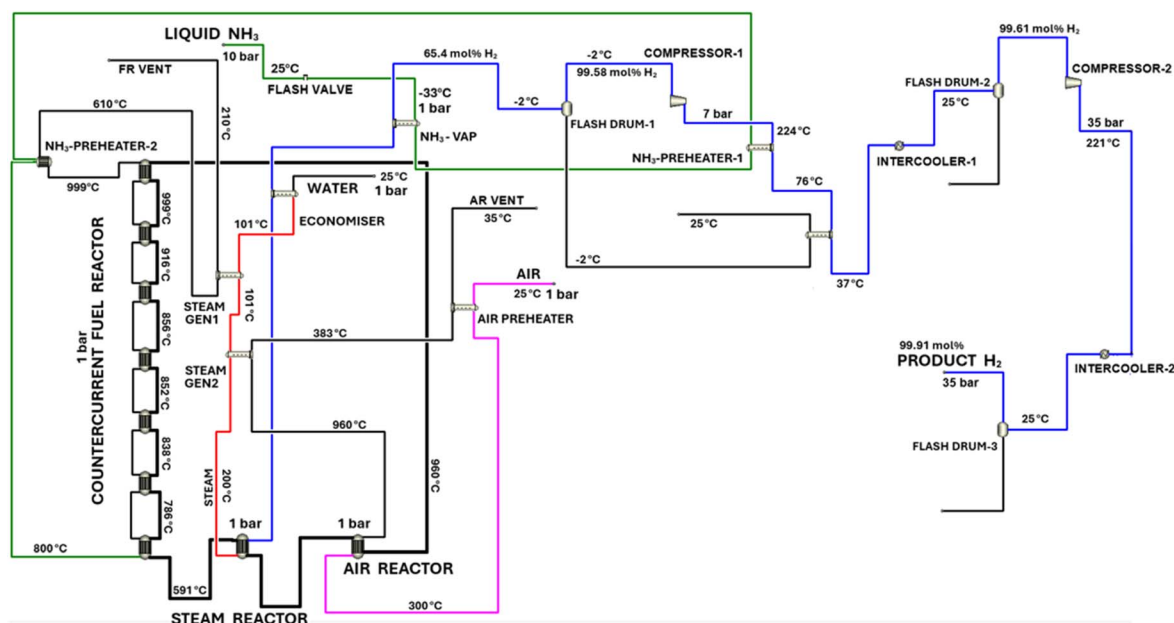


Fig. 3 Schematic diagram of the Aspen Plus model with  $T_{Ao} = 960$   $^\circ\text{C}$ .



of  $H_2$  production of approximately  $200 \text{ kg h}^{-1}$ , capacity suitable for applications in hydrogen refuelling stations or for on-site fuel cells.

As  $T_{A0}$  increases,  $E_{red}$  increases due to thermodynamic favourability.<sup>45</sup>  $Y_{H_2}$  increases when  $T_{A0}$  increases from  $880^\circ\text{C}$  to  $890^\circ\text{C}$ , however, it stabilises and decreases when  $T_{A0}$  increases further from  $960^\circ\text{C}$ . It can be observed that  $T_{F0}$  and  $T_{S0}$  increase with  $T_{A0}$ , but there is a significant decrease when  $T_{A0}$  is around  $960^\circ\text{C}$ . Meanwhile,  $W_{Fe_{0.947}O}$  suddenly increases from zero when  $T_{A0}$  rises above  $960^\circ\text{C}$ , while  $W_{Fe}$  drops to zero. When  $T_{A0}$  is at  $960^\circ\text{C}$ ,  $T_{F0}$  is about  $590^\circ\text{C}$ , which corresponds to the disproportionation temperature of iron oxide. The phase diagram of iron oxides with the presence of steam shows that the Wustite phase ( $Fe_{0.947}O$ ) appears when the SR temperature is above the disproportionation temperature.<sup>46</sup> Below this temperature, Fe can be directly oxidised to  $Fe_3O_4$ , so the fuel reactor (FR) and the steam reactor (SR) are in the  $Fe \leftrightarrow Fe_3O_4$  phase equilibria. This explains the sudden increase in  $W_{Fe_{0.947}O}$  as the equilibria shifts from  $Fe \leftrightarrow Fe_3O_4$  to  $Fe \leftrightarrow Fe_{0.947}O \leftrightarrow Fe_3O_4$  when  $T_{A0}$  exceeds  $960^\circ\text{C}$ .

$H_2$  in the FR vent ( $V_{H_2}$ ) decreases as  $T_{A0}$  increases up to  $960^\circ\text{C}$  and then remains almost zero when the  $T_{A0}$  is greater than  $960^\circ\text{C}$ , meaning that no hydrogen is produced in the FR. This may be due to the increase in the reduction rate in the FR until the peak value at  $590^\circ\text{C}$  ( $T_{F0}$ ). In terms of  $E_{red}$ , about 11% (calculation is shown in SI) of  $Fe_2O_3$  in the FR is unutilised due to the thermodynamic barrier in re-oxidation in the SR.<sup>47</sup> In other words, only 89%  $Fe_2O_3$  contributes to the production of  $Y_{H_2}$  in the process. When  $T_{A0}$  increases from  $880$  to  $960^\circ\text{C}$ ,  $W_{Fe}$  increases, and more Fe converts to  $Fe_3O_4$  in the SR. This explains why  $Y_{H_2}$  remains stable when  $E_{red}$  increases. However, the conversion between  $Fe_{0.947}O$  and  $Fe_3O_4$  in the SR results in a lower  $Y_{H_2}$  when  $T_{A0}$  is above  $960^\circ\text{C}$ .

On the other hand,  $S_{steam}$  and  $S_{air}$  increase as  $T_{A0}$  increases, while  $X_{H_2}$  decreases. The increase in  $S_{steam}$  with  $T_{A0}$  is due to the rise in  $T_{F0}$ . With a constant total ammonia feed rate ( $M_{NH_3}$ ), the endothermic heat requirement remains unchanged, which causes excess heat carry-over in the reduced iron oxides to the SR. A higher  $T_{F0}$  results in a lower steam equilibrium conversion, indicating that more steam is needed to sustain the oxidation of the reduced iron oxides.<sup>39</sup> Due to an increased  $S_{steam}$ ,  $X_{H_2}$  decreases as  $T_{A0}$  rises. The  $NH_3$  CLCr process conceptualised in this work consists of an energy-intensive steam production step, which consumes 50–60% of all recovered heat. Additionally, the high steam mass fraction in the SR outlet ( $1 - X_{H_2}$ ) raises the latent heat load, limiting the extent of gas cooling and condensation in the ammonia vaporiser. This results in more compression work in the purification section, due to higher average gas molar mass resulting from higher moisture content in the gas exiting the vaporiser. The step changes can be observed when  $T_{A0}$  is around  $960^\circ\text{C}$  for all the three parameters mentioned above. As mentioned previously, the equilibria shift from  $Fe \leftrightarrow Fe_3O_4$  to  $Fe \leftrightarrow Fe_{0.947}O \leftrightarrow Fe_3O_4$  leads to significant increases the  $P_{H_2O}/P_{H_2}$  requirement in the SR, which in turn results in a higher steam consumption and lower  $X_{H_2}$ . When  $T_{A0}$  is lower than  $960^\circ\text{C}$ ,  $S_{air}$  increases as more  $W_{Fe}$  requirement in the AR. When  $T_{A0}$  is higher than  $960^\circ\text{C}$ ,  $S_{air}$  increases as more

$Fe_{0.947}O$  is required to enable a higher reaction temperature in the AR, which compromises the conversion of  $Fe_3O_4$  to  $Fe_{0.947}O$  in the SR.

### Effect of FR outlet temperature ( $T_{F0}$ )

In this section, the inlet oxide feed for the converged model (Fig. 3) when  $T_{A0}$  is  $960^\circ\text{C}$  was applied ( $Fe_{0.947}O$  61.58%, Fe 11.56%, balanced by  $Al_2O_3$ ). With an  $M_{NH_3}$  of  $1380 \text{ kg h}^{-1}$ , the maximum hydrogen generation ( $\dot{m}_{H_2, \text{max}}$ ) is  $186.9 \text{ kg h}^{-1}$  (calculation shown in Supplementary Information). The effect of  $T_{F0}$  within the range of  $150$ – $900^\circ\text{C}$  was evaluated. In addition to  $T_{F0}$ , the steam flow between  $1000$  and  $4000 \text{ kg h}^{-1}$  was also considered.

The results are presented in the form of a mesh plot, showing the flow rate of hydrogen ( $M_{H_2}$ ) at various  $T_{F0}$  and steam flow (Fig. 5). The six areas highlighted by the dashed lines represent different states of equilibria inside the SR. Area 6 shows the steam flow rate at different  $T_{F0}$  to reach the maximum hydrogen generation ( $\dot{m}_{H_2, \text{max}} = 186.9 \text{ kg h}^{-1}$ ). When  $M_{H_2}$  is constant (the horizontal lines shown in Fig. 5), more steam is consumed as  $T_{F0}$  increases. The specific steam consumption ( $S_{steam}$ ) increases as steam is consumed faster at higher  $T_{F0}$ . Area 1 illustrates the scenario with low  $S_{steam}$ . At this stage, the system in the SR is in the  $Fe \leftrightarrow Fe_3O_4$  phase equilibria, where lower  $P_{H_2O}/P_{H_2}$  is required for the conversion.<sup>46</sup> This scenario (high  $M_{H_2}$  achieved at low  $T_{F0}$ ) seems advantageous, but Collins-Martinez *et al.* advised a minimum  $T_{F0}$  of  $400^\circ\text{C}$  in the SR to avoid slow kinetics.<sup>39</sup> When  $T_{F0}$  is higher than the

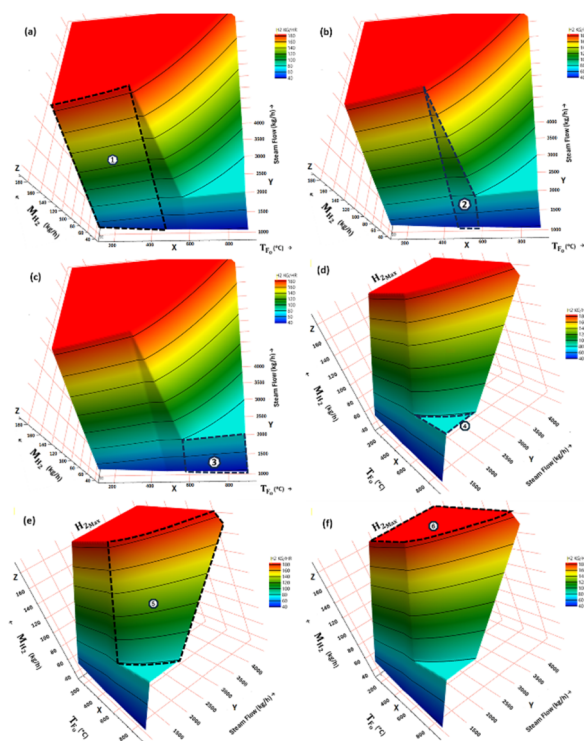


Fig. 5 Mesh plots of hydrogen production ( $M_{H_2}$ ) as a function of fuel reactor outlet temperature ( $T_{F0}$ ) and steam flow at  $T_{A0} = 960^\circ\text{C}$ , with six highlighted areas.



disproportionation temperature ( $\sim 590^\circ\text{C}$ ), a stable hydrogen flowrate ( $80.6\text{ kg h}^{-1}$ ) can be observed at low steam flowrate (area 4) (calculation shown in Supplementary Information). As the specific steam flow rate ( $S_{\text{steam}}$ ) increases, the hydrogen flow rate increases significantly (area 5). At low  $S_{\text{steam}}$ , the hydrogen is generated from Fe-phase only (area 3). Hydrogen generated solely from the Fe-phase reaches its maximum ( $80.6\text{ kg.h}^{-1}$ ) at area 4. By increasing  $S_{\text{steam}}$ , and there by  $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$ , the equilibria shifts from  $\text{Fe} \leftrightarrow \text{Fe}_3\text{O}_4$  to  $\text{Fe} \leftrightarrow \text{Fe}_{0.947}\text{O} \leftrightarrow \text{Fe}_3\text{O}_4$  (area 5), in which the  $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$  requirement for  $\text{Fe}_{0.947}\text{O} \leftrightarrow \text{Fe}_3\text{O}_4$  is much higher than the previous step ( $\text{Fe} \leftrightarrow \text{Fe}_{0.947}\text{O}$ ). As the temperature increases, the  $\text{Fe}_{0.947}\text{O} \rightarrow \text{Fe}_3\text{O}_4$  transition become non-spontaneous, meaning higher  $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$  or higher  $S_{\text{steam}}$  is needed to shift the equilibrium to the right.<sup>48</sup> However, area 2 shows inconsistent behaviour in the SR when  $T_{\text{Fo}}$  is between  $450^\circ\text{C}$  and the disproportionation temperature ( $590^\circ\text{C}$ ).  $S_{\text{steam}}$  slightly increases when  $T_{\text{Fo}}$  drops from  $590^\circ\text{C}$  to  $450^\circ\text{C}$ . Gleeson *et al.* stated that the  $\text{Fe}_{0.947}\text{O}$  phase was thermodynamically stable beyond  $590^\circ\text{C}$ , and the reduction shifts from  $\text{Fe} \leftrightarrow \text{Fe}_{0.947}\text{O} \leftrightarrow \text{Fe}_3\text{O}_4$  to  $\text{Fe} \leftrightarrow \text{Fe}_3\text{O}_4$  below  $590^\circ\text{C}$ .<sup>49</sup> Herein, the exothermic disproportionation reaction (eqn (9)) occurs below  $590^\circ\text{C}$ . The released heat from the reaction (eqn (9)) results in an increase in temperature. At higher  $S_{\text{steam}}$ , less  $\text{Fe}_{0.947}\text{O}$  is available for the disproportionation as  $\text{Fe}_{0.947}\text{O}$  converts to Fe in the SR when  $M_{\text{H}_2}$  is higher. Thus,  $T_{\text{Fo}}$  has insignificant influences on the hydrogen generation (area 2 shrinks).

### Effect of ammonia to OC ratio ( $R_{\text{NH}_3/\text{OC}}$ )

Fig. 6 shows the effect of  $R_{\text{NH}_3/\text{OC}}$  on the performance of the CLCr process. In this study, the OC flow rate is  $20\,000\text{ kg h}^{-1}$  and the ammonia flow rates vary from  $1000$  to  $1900\text{ kg h}^{-1}$  in order to achieve an ammonia to OC ratio ( $R_{\text{NH}_3/\text{OC}}$ ) of  $10.5$ – $20$ . The AR outlet is fully oxidised at  $960^\circ\text{C}$  under stoichiometric air flow conditions.

As can be seen from Fig. 6, the flow rate of the feed ammonia has an effect on the overall performance of the process. As  $R_{\text{NH}_3/\text{OC}}$  increases,  $Y_{\text{H}_2}$  and  $E_{\text{red}}$  in FR increase.  $T_{\text{Fo}}$  and  $T_{\text{So}}$  drops continuously as the heat demand in the FR increases. As

mentioned previously,  $\text{Fe}_{0.947}\text{O}$  disproportionation occurs when  $T_{\text{Fo}}$  falls to  $590^\circ\text{C}$ . Therefore,  $X_{\text{Fe}_3\text{O}_4}$  and  $X_{\text{Fe}}$  increase significantly as the phase equilibria shifts from  $\text{Fe}_3\text{O}_4 \leftrightarrow \text{Fe}_{0.947}\text{O} \leftrightarrow \text{Fe}$  to  $\text{Fe}_3\text{O}_4 \leftrightarrow \text{Fe}$  in the FR, while  $X_{\text{Fe}_{0.947}\text{O}}$  significantly decreases. The exothermic reaction (eqn (9)) leads to a sudden rise in  $T_{\text{Fo}}$ . All the hydrogen from ammonia decomposition is consumed until  $T_{\text{Fo}}$  reaches  $590^\circ\text{C}$ . When the disproportionation occurs,  $V_{\text{H}_2}$  increases with  $R_{\text{NH}_3/\text{OC}}$ . The reduction rate of  $\text{Fe}_3\text{O}_4$  was found to be maximum at approximately  $580^\circ\text{C}$ , when magnetite was used, and an  $E_{\text{red}}$  of  $20$ – $60\%$  was applied.<sup>50</sup> Herein, the increase of  $V_{\text{H}_2}$  is due to the drop in reduction rates. This also explains the slower increase in  $E_{\text{red}}$  once  $T_{\text{Fo}}$  decreases to  $590^\circ\text{C}$ . The disproportionation in the SR leads to a sudden increase in  $T_{\text{So}}$ , which aligns with the observations mentioned previous section, as  $S_{\text{steam}}$  increases below  $590^\circ\text{C}$ . When  $T_{\text{Ao}}$  is at  $960^\circ\text{C}$  and  $T_{\text{Fo}}$  is close to  $590^\circ\text{C}$ , the value of  $R_{\text{NH}_3/\text{OC}}$  should be  $\sim 14.5$  to achieve the optimal  $E_{\text{red}}$  and hydrogen utilisation in the FR.

### Effect of steam reactor pressure

The pressure has no effect on the hydrogen yield, as the gas ratios in the SR are equimolar.<sup>51</sup> However, high pressures in the SR can reduce the power of the compressor in the subsequent hydrogen compression stage. An SR pressure in the range of  $1$ – $15$  bars was studied, and their performance was compared and summarised in Table 5 (calculations shown in SI).

The cold gas efficiency slightly decreases as the SR pressure increases, with a reduced conversion of  $\text{Fe}_{0.947}\text{O}$ . The temperature rise in the SR decreases, indicating a reduced heat of the reaction. As a result, the mass fraction of  $\text{Fe}_{0.947}\text{O}$  increases with the pressure. The pressure shows a limited impact on the overall performance. Similar trends were reported in previous literature on syngas cracking in CL.<sup>52</sup> There is no correlation between pressure and hydrogen purity in the SR vent, which was validated by experiments, as hydrogen purities are beyond  $99.99\%$  at higher pressures.

Clearly, the power requirement of the subsequent hydrogen compression can be eliminated when the pressure is above  $5$  bar, as water condensation is improved by elevating the dew points. This also enhances the latent heat consumption, resulting in an increase in the overall energy efficiency.

### Model optimisation

**Determination of the optimal operating temperature ( $\Delta_{\text{Optimal}}$ ).** The objective of the model optimisation process is to determine the optimal operating temperature ( $\Delta_{\text{Optimal}}$ ) for  $T_{\text{Ao}}$ ,

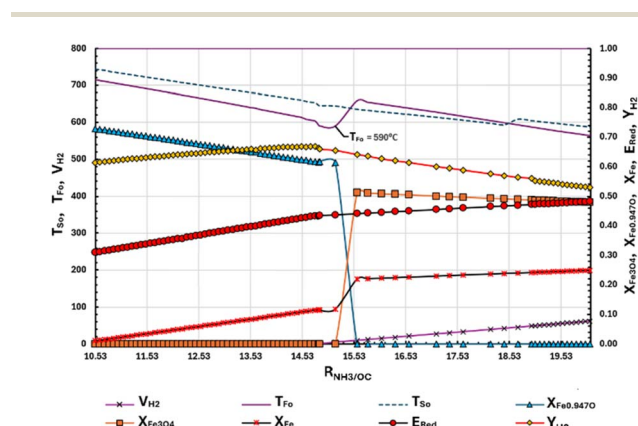


Fig. 6 Effect of  $R_{\text{NH}_3/\text{OC}}$  on hydrogen yield ( $Y_{\text{H}_2}$ ), extent of reduction ( $E_{\text{red}}$ ), mass fractions of  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_{0.947}\text{O}$  and Fe in reduced oxides ( $X_{\text{Fe}_3\text{O}_4}$ ,  $X_{\text{Fe}_{0.947}\text{O}}$ ,  $X_{\text{Fe}}$ ), unutilised  $\text{H}_2$  in the FR vent ( $V_{\text{H}_2}$ ), SR outlet temperature ( $T_{\text{So}}$ ), and FR outlet temperature ( $T_{\text{Fo}}$ ).

Table 5 Performance with SR pressure varying from 1 to 15 bars

| Parameter                                                        | 1 bar | 5 bar  | 10 bar | 15 bar |
|------------------------------------------------------------------|-------|--------|--------|--------|
| $\eta_{\text{CGE}}$ (%)                                          | 74.19 | 74.13  | 74.03  | 73.95  |
| $\eta_{\text{OEE}}$ (%)                                          | 69.07 | 75.51  | 75.41  | 75.33  |
| Hydrogen purity (% mol mol <sup>-1</sup> )                       | 99.91 | >99.99 | >99.99 | >99.99 |
| $W_{\text{Fe}_{0.947}\text{O}}$ (wt%)                            | 12.5  | 12.6   | 12.7   | 12.9   |
| $\Delta T_{\text{SR}}$ ( $^\circ\text{C kmol}^{-1}\text{-O}_2$ ) | 1.314 | 1.294  | 1.267  | 1.24   |
| $W_{\text{comp}}$ (kWh)                                          | 307   | 0      | 0      | 0      |



under which an autothermal condition is achieved with the optimal value of the overall energy efficiency ( $\eta_{OEE}$ ) and high hydrogen yield ( $Y_{H_2}$ ). The simulations were carried out by varying the AR outlet temperature ( $T_{Ao}$ ) and the ammonia to OC ratio ( $R_{NH_3/OC}$ ). The  $R_{NH_3/OC}$  was adjusted to achieve the highest  $E_{red}$  at each  $T_{Ao}$  (880–1050 °C).

A few assumptions were made: (1) the unutilised hydrogen ( $V_{H_2}$ ) for the FR is negligible to maximise hydrogen yield; (2) the FR outlet temperature ( $T_{Fo}$ ) was maintained to be close to 590 °C to exhibit stable phase equilibria; and (3) all reactions in the AR and the SR are stoichiometric.

As shown in Fig. 7, when  $T_{Ao}$  is around 900 °C and  $R_{NH_3/OC}$  is 13.60,  $\eta_{OEE}$  reaches its maximum value (71.7%). When  $T_{Ao}$  is 880 or 890 °C,  $Y_{H_2}$  is equal to the theoretical maximum hydrogen yield ( $Y_{H_2, max}$ ) but with a sacrifice of  $\eta_{OEE}$ . At  $T_{Ao} = 900$  °C,  $Y_{H_2}$  starts to drop continuously due to the increase in  $E_{red}$ . In terms of the fraction of fuel energy lost as heat ( $F_L$ ), the system exhibits a lower loss at  $T_{Ao}$  of 900 °C. Therefore,  $T_{Ao}$  of 900 °C was selected for the following process intensification.

**Process intensification.** The aim of process intensification is to further improve the overall energy efficiency ( $\eta_{OEE}$ ) and the hydrogen yield ( $Y_{H_2}$ ) through the extent of reduction ( $E_{red}$ ), with a minimised loss of fuel energy as heat ( $F_L$ ) for high-purity hydrogen production (with  $T_{Ao} = 900$  °C). As described in the previous section, the energy demand of the compressor ( $W_{comp}$ ) can be eliminated when the SR pressure is equal to 5 bar. On the other hand, the power requirement for pressurised water ( $W_{pump}$ ) is 0.31 kWh. Therefore,  $\eta_{OEE}$  significantly increases while  $F_L$  reduces, achieving 78.2% and 17.8%, respectively. At this stage, the purity of hydrogen is above 99.99%. In an autothermal process, external energy consumption is zero. The

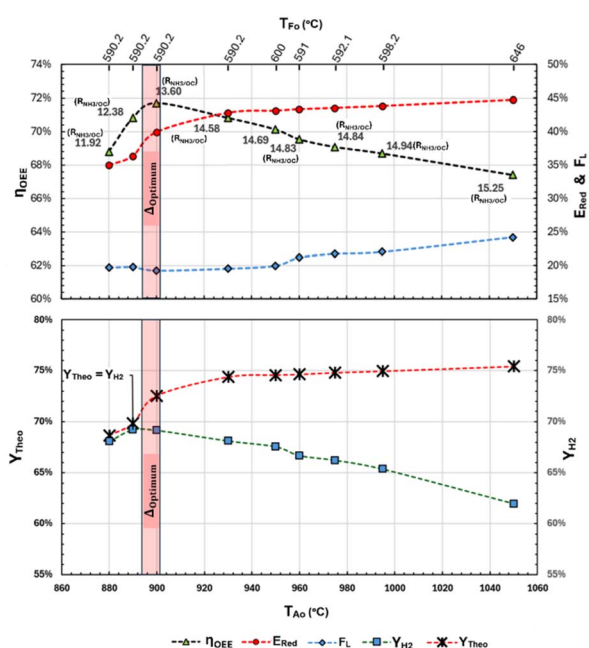


Fig. 7 Comparison of the extent of reduction ( $E_{red}$ ), fractional ammonia fuel energy loss ( $F_L$ ), overall energy efficiency ( $\eta_{OEE}$ ), theoretical maximum  $H_2$  yield ( $Y_{Theo}$ ), and actual  $H_2$  yield ( $Y_{H_2}$ ) for  $T_{Ao}$  varying from 880–1050 °C and  $R_{NH_3/OC}$  varying from 11.92 to 15.25.

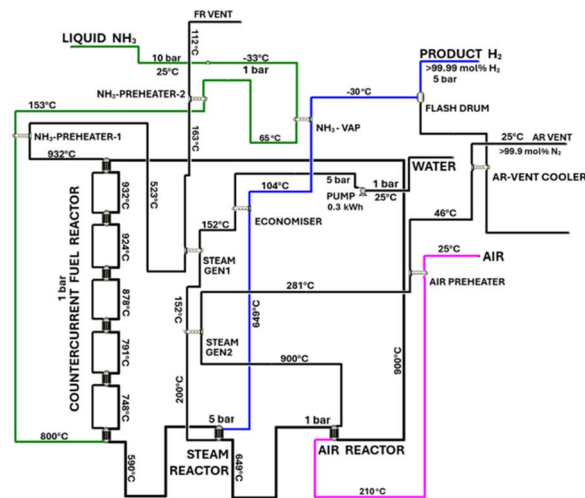


Fig. 8 Schematic diagram of the optimised model with key operating conditions.

temperature of preheated air can be reduced to 210 °C as the steam latent heat load decreases in the ammonia vaporiser. The key operating condition of the intensified process is presented in Fig. 8. Under the optimised conditions, the overall energy efficiency ( $\eta_{OEE}$ ) reaches 79.6%, with a hydrogen yield ( $Y_{H_2}$ ) of 69.4%.

### Thermodynamic performance analysis of the optimised model

**Heat balance.** Table 6 presents the results from the heat calculations for the optimised model (Fig. 8). Details of the calculations can be found in Supplementary Information. As shown in Table 6, the net heat consumed is 9349.6 MJ h<sup>-1</sup>, while the net heat generated is 9497.8 MJ h<sup>-1</sup>, confirming that the CLCr process is autothermal.

**Exergy analysis.** The total exergy of the inlet and outlet streams (in MJ h<sup>-1</sup>) was calculated using eqn (27) and (28), with the results summarised in Table 7. The total exergy of the inlet and outlet streams are 24 770.9 MJ h<sup>-1</sup> and 19 400.5 MJ h<sup>-1</sup>, respectively, with an overall exergy efficiency ( $\eta_e$ ) of 70.4% (calculated using eqn (26)). Of the total unused exergy, about 71.6% was destroyed during the CLCr process (e.g., high irreversibility of the reactions), and the other 28.4% was wasted in the exhaust streams (spent air and FR vent).<sup>53</sup> The exergy

Table 6 Net heat demands in the heat sink and heat sources in MJ h<sup>-1</sup>

|              | In                              |          | Total    |
|--------------|---------------------------------|----------|----------|
| Heat sink    | From FR inlet (feed oxides)     | 27 400   | 27 737.8 |
|              | From ammonia (feed ammonia)     | 337.8    |          |
|              | Out                             |          |          |
|              | From FR outlet (reduced oxides) | 11 073.1 | 18 388.2 |
| Heat sources | From process                    | 7315.1   |          |
|              | Heat sink balance (in-out)      |          | 9349.6   |
|              | $\Delta H_{CombNH_3-fuel}^0$    | 8740.1   | 9497.8   |
|              | $\Delta H_{SR}^0$               | 757.7    |          |
|              | Heat sources balance            |          | 9497.8   |





Table 7 Exergy of the inlet and outlet streams

|        | Streams           | Physical exergy | Chemical exergy | Total exergy |
|--------|-------------------|-----------------|-----------------|--------------|
| Inlet  | Ammonia           | 392.4           | 24 170          | 24 562.4     |
|        | Air               | −2.7            | 109.3           | 106.6        |
|        | Water             | 0               | 101.9           | 101.9        |
| Outlet | Fuel reactor vent | 813.5           | 957.2           | 1770.7       |
|        | SR vent           | 314.2           | 0               | 314.2        |
|        | Air reactor vent  | −2.1            | 42.7            | 40.6         |
|        | Removed water     | 0               | −0.4            | −0.4         |
|        | Product hydrogen  | 0               | 17 275.4        | 17 275.4     |

destruction mainly arises from the irreversibility of the redox reactions of the Fe-based OC. The extent of irreversibility could be reduced by employing alternative OCs, or combining Fe-based OC with materials with narrower thermodynamic gaps between the reduction and oxidation steps, such as mixed oxides-based materials (e.g.,  $\text{CeO}_2$ ).<sup>54,55</sup> Further exergy reduction could be achieved through enhanced heat recovery or advanced reactor design for better temperature control.

**Techno-economic analysis.** To evaluate the economic viability of the proposed system, a preliminary techno-economic analysis (TEA) was carried out to estimate the cost of the hydrogen produced from the process and identify key contributors to its cost. As a detailed TEA is not the main focus of this study, the calculation methodology, assumptions, and supporting data are provided in the Supplementary Information file.

The levelised cost of hydrogen (LCOH) estimated from the purchased equipment cost was  $\$4.61 \text{ kg}^{-1}$  with the optimised case and the price of the feed ammonia being  $\$0.47 \text{ kg}^{-1}$ .<sup>56</sup> The price of the feed ammonia was identified to be the largest contributor to the LCOH (84.4%), followed by annual capital expenditure (12.2%), variable operating capital (2.2%), and fixed operating capital (1.1%). The proposed process shows good potential in terms of economic viability, in line with findings from large-scale green ammonia decomposition studies reporting an LCOH of  $\$5.1 \text{ kg}^{-1}$ ,<sup>57</sup> which can be further reduced to  $\$3.4 \text{ kg}^{-1}$  with a cheaper ammonia cost of  $\$0.25 \text{ kg}^{-1}$ .

## Limitations and future work

Although there are existing studies on CL  $\text{CH}_4$  cracking for hydrogen production,<sup>58</sup> CL  $\text{NH}_3$  synthesis,<sup>59</sup> and syngas production with  $\text{NH}_3$  and  $\text{CO}_2$  through CL,<sup>60</sup> to the best of the authors' knowledge, this work is the first attempt to model and evaluate a CL system for hydrogen production through  $\text{NH}_3$  cracking using Fe-based oxygen carriers. While the thermodynamic modelling in this study successfully demonstrated the potential of the proposed  $\text{NH}_3$  CLCr process, several limitations of this work should be acknowledged. First, the simulations were carried out under equilibrium assumptions without explicit consideration of reaction kinetics or mass transfer limitations. Incorporating kinetic models into future simulations will better capture the iron oxide redox cycles and  $\text{NH}_3$  conversion, especially at lower operating conditions. Second,

some practical material and operational challenges still remain. The long-term durability of iron oxides under repeated cycling may be impaired due to sintering and potential formation of iron nitride species.<sup>61</sup> Experimental studies of iron oxides under an  $\text{NH}_3$  environment is needed as part of the future work to provide useful information on the stability of the Fe-based OCs. Finally, the development of OCs with smaller irreversibility of the redox reactions, and better heat integration are needed.<sup>62</sup>

## Conclusions

In this study, a novel ammonia cracking chemical looping process for high-purity hydrogen production was designed and evaluated through process modelling and thermodynamic analysis. Iron oxide was selected as the oxygen carrier. A parametric study was carried out to evaluate the effect of key operating conditions on the process performance. The results demonstrated that an AR outlet temperature of  $960^\circ\text{C}$ , an FR outlet temperature of  $590^\circ\text{C}$ , and an ammonia to OC carrier ratio of 14.5 provided optimal conditions for maximising hydrogen yield and energy efficiency, while minimising process energy losses. Process intensification strategies, such as increasing the SR pressure to 5 bar, can help achieve an overall energy efficiency of 78%, exergy efficiency of 70.9%, and a hydrogen yield of 69.4% with a purity above 99.99%. Under steady operation, the process is autothermal, without the requirement of external heating. These findings highlight the potential of the CLCr process as a scalable and energy-efficient method for producing high-purity hydrogen from ammonia. This study paves the way for further experimental validation to assess the reaction kinetics and oxygen carrier stability, as well as techno-economic analysis to evaluate its feasibility for industrial-scale implementation.

## Author contributions

Anantha Krishnan Vinayak Soman: formal analysis, data curation, writing – original draft. Siqi Wang: formal analysis, data curation, writing – original draft. Ziqi Shen: formal analysis, writing – original draft. Mingming Zhu: funding acquisition, conceptualisation, supervision, writing – review & editing.

## Conflicts of interest

There are no conflicts to declare.



## Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: detailed calculation of heat balance and techno-economic analysis. See DOI: <https://doi.org/10.1039/d5se01010a>.

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