**MODELING AND ANALYSIS**

Multi-objective optimization of green urea production

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Abstract

The availability of natural gas as feedstock for nitrogen fertilizer production continues to decline, while its price increases, encouraging the search for renewable feedstocks for the future green urea industry. Renewable feedstocks include waste biomass, hydrogen from solar PV-electrolysis, and the combination of these feedstocks with natural gas. The selection of a green production strategy is a critical step in the trade-off between economic and environmental considerations. The aim of this work was to propose a green urea production strategy using a multi-objective optimization (MOO) model to minimize production costs and environmental impacts by considering the future cost development of technologies and feedstock price for each technology in the time frame of 2020-2050. The results show that green urea production can reduce production costs and greenhouse gas emissions, compared to conventional urea production. Biomass gasification technology fulfills the minimum requirements for production cost and CO₂ emissions from 2020 to 2035 and combined biomass gasification-PV electrolysis without battery technology is the optimum process from 2040 to 2050.

KEYWORDS

green urea, hydrogen, multi-objective optimization

1 | INTRODUCTION

In the nitrogen fertilizer industry, hydrogen is an important component of an ammonia-forming compound, which is used as a raw material of urea. In the process of making ammonia and urea, hydrogen is produced through the steam methane reforming (SMR) process, in which methane and steam react to produce carbon monoxide and hydrogen. This type of reaction is highly endothermic, requiring external energy when reacting.

Due to limited natural gas reserves and price increases, it is necessary to find alternative sources of hydrogen. Hydrogen can serve as an intermediate product of ammonia and urea plants through biomass gasification and PV electrolysis of water.

Research on green chemistry focuses on the development of chemical products and processes, mostly involving waste minimization, replacement of existing products with less

toxic alternatives, and a shift toward renewable feedstocks. The chemical industry is currently searching for innovative ways of reducing greenhouse gas emissions (GHG) associated with the production of ammonia, to replace the century-old Haber-Bosch process of manufacturing ammonia from N₂ and H₂. Nitrogen fertilizers manufactured using wind power were developed; wind-based ammonia production can significantly decrease fossil energy input and GHG compared to the conventional production.¹ Other studies have focused on the production of ammonia through wind-generated electricity at a remote island, utilizing all the excess wind power that was not needed to meet the load demand for ammonia synthesis,² and the greening of ammonia, using a solar ammonia refinery, which utilizes solar energy for the process of ammonia production.³ There is a developed method for energy evaluation of different renewable energy sources,

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integrated in ammonia production plants that can be obtained from biomass gasification, biogas reforming, or electrolysis of water with electricity generated by solar or wind energy.⁴ Electrochemical ammonia production has been developed to substantially reduce the energy input by more than 20%, simplify the reactor design, and reduce the complexity and cost of the plant when compared with the conventional ammonia production route.⁵ There is a developed model of multi-objective optimization (MOO) for biomass-based ammonia production, a potential application in which biomass feedstock can replace fossil fuel feedstock in ammonia production;⁶ however, this study did not take account multiyear perspective and the renewable energy source was limited to only biomass feedstock. MOO of renewable ammonia from water and air has been developed by Sanchez and Martin,⁷ with the full process formulated as an MINLP problem; however, this study did not take into account the learning curve of capital expenditure of PV and Wind Turbine.

Research on MOO of the utilization of renewable energy into green chemical products has been limited to the manufacturing of methanol, ammonia, and methane on a single year basis. To our knowledge, there is no MOO of the utilization of renewable energy and the combination of its processes as a feedstock for green urea production on multiyear periods by taking into account the learning curve of capital expenditure for minimizing both production cost and CO₂ emission.

The aim of this study was to develop a MOO model for long-term green urea production, to assess the economic and environmental effects, and to identify an optimal production strategy for more sustainable urea production.

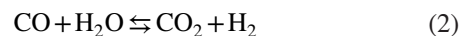
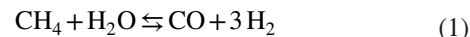
2 | GREEN PRODUCTION PATHWAY

2.1 | Hydrogen production technologies

Hydrogen poses as an energy alternative from abundant available resources while reducing carbon emissions. However, it does not exist naturally in molecular form. It must be produced from a diversity of feedstock sources, such as fossil fuels, water, and biomass, but it requires a huge amount of energy to convert it to pure hydrogen. This short review on hydrogen production is focused on commercial uses and the near-term and medium-term market readiness of processes such as reforming of hydrocarbon, biomass gasification, and PV electrolysis.

There are several commercial technologies available for producing hydrogen from fossil fuels. Currently, most of commercially produced hydrogen (96%) comes from fossil fuels, with 48% of that proportion from natural gas, 30% from heavy oils and naphtha, and 18% from coal. Only 4% of the hydrogen produced is obtained by means of water electrolysis.⁸ Hydrogen from natural gas consists of different conversion

routes: SMR, partial oxidation (POX), and dry reforming (DR) with various ratios of H₂/CO. For ammonia/urea production, SMR is the most suitable process due to synthesis gas produced with highest hydrogen to carbon monoxide ratio. It is considered ideal to be used as feedstock in the petrochemical industries. Carbon monoxide can be further converted to hydrogen and carbon dioxide through the water-gas shift (WGS).



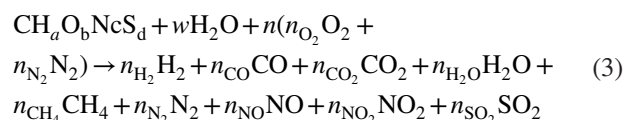
The process typically occurs at temperatures of 700-850°C and pressures of 30-35 bars. The overall process is highly endothermic, requiring large amounts of energy. The energy required is typically supplied by natural gas combustion (up to ~30%). Steam reforming of methane is widely used in industry today for large centralized plants in chemical manufacturing. Partial oxidation, DR, and autothermal reforming (combining SMR and POX) also perform as options to produce syngas with the value of the H₂/CO ratio that is required and to reduce energy consumption.⁹

For renewable-based hydrogen production, gasification technology is an efficient way to produce H₂ from biomass. Particularly, coal gasification had been used for years before natural gas reforming. The biomass gasification process has been widely studied and the technology has been developed for several reasons, such as the availability of biomass resources, producing a mixture of combustible gases that can be used as fuels, or as intermediate products in the large-scale production of fuels and chemicals.¹⁰

Biomass gasification is usually carried out at temperatures of 700-1200°C, using air, oxygen, steam, or their mixtures as gasifying agents, which leads to a mixture of gaseous products composed of mainly syngas (mixture H₂ and CO), CO₂, CH₄, and other hydrocarbons.¹¹ The use of steam as a gasifying agent serves to increase H₂ composition and produce gases with high heating value, absent of nitrogen. As the highly endothermic character of steam gasification increases the cost of energy compared to air gasification, it needs a costly oxygen separation process. In this study, air-steam biomass gasification is used on account of the trade-off between energy consumption and hydrogen composition.

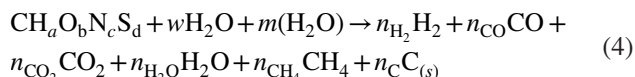
The principal processes of biomass steam gasification are drying, pyrolysis, char gasification, and homogeneous reactions undergone by pyrolysis volatiles, that is, cracking, reforming, and WGS.

The global gasification reaction for biomass gasification with air, oxygen, and oxygen-enriched air can be expressed as¹²:

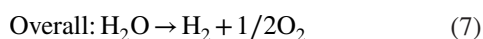
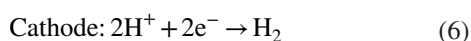
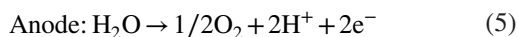


where $\text{CH}_a\text{O}_b\text{N}_c\text{S}_d$ denotes the biomass fuel, w is the biomass moisture content, and n is the kilomoles of agent per kilomoles of biomass entering the gasifier.

For steam biomass gasification, the reaction has been summarized as the following¹²:



Water electrolysis is the process where water is split into hydrogen and oxygen through the application of electrical energy. In the water electrolysis process, water is the reactant, which is dissociated into hydrogen and oxygen under the influence of a direct current.



Different electrolyte systems developed for water electrolysis include alkaline water electrolysis (AWE), proton exchange membranes (PEMs), and solid oxide water electrolysis (SOE).¹³ This study focuses on electrical energy-based hydrogen production using PV electricity and the well-developed technology of water electrolysis at low temperatures called PEM electrolysis, as it is more environmentally friendly and has fast response, high efficiency, compact design, and high output pressure. The operating current density of this system was much higher than that of other AWE technologies. Additionally, balancing PEM electrolysis plants is much simpler, which is more attractive for industrial applications. However, the costs of the electrocatalysts are more expensive.^{14,15}

For electricity generation, the renewable nature of the PV electricity along with its large resource potential especially for tropical countries¹⁶ and cost reduction has motivated a fast deployment of PV electricity plants in recent years.¹⁷

Although hydrocarbons are currently the main feedstock used for H_2 production for urea, green urea production routes through an integration of renewable-technology-based hydrogen production in fossil-based technology will become unavoidable. With the decline in fossil fuels and increased attention toward the greenhouse effect, the share of renewable technologies will increase in the near future, while, in the long term, they are expected to dominate over conventional technologies.

2.2 | Process technology selection

This study is based on an existing nitrogen fertilizer plant located in East Kalimantan in Borneo Island. East Kalimantan is used as a case study because it has a conventional urea plant that has been operating since 1977 and natural gas reserves in the area are declining. For development of sustainable urea, diversification of feedstock is required. Moreover, East Kalimantan lies on equator area which is rich in renewable energy resources.

The process technology selection related to alternative feedstock is based on criteria for scoring such as production cost, CO_2 emissions per unit product, maturity level of the technology, energy efficiency of the process, and production scale of hydrogen manufacturing. It should be noted that because the location of the urea industry is in Borneo, the geothermal, hydropower, and wind turbine technologies were not selected because of their small potentials.

From the selection process, the potential technology candidates were steam reforming of methane, biomass gasification, PV electrolysis, and the combination of these technologies. Thus, the final process path chosen for optimization is as follows: Steam Reforming of methane (SR), Biomass Gasification (BG), PV Electrolysis (PV EIB), Combine Steam Reforming-Biomass Gasification (SR-BG), Combine Steam Reforming-PV Electrolysis with battery (SR-PV EIB), Combine Biomass Gasification-PV Electrolysis (BG-PV EIB), Combine Steam Methane Reforming-PV Electrolysis without battery (SR-PV EI), and Combine Biomass Gasification-PV Electrolysis without battery (BG-PV EI).

Figure 1 shows the block flow diagram of green urea production using renewable feedstocks and methane. Each steam reforming, biomass gasification, and PV electrolysis process will produce gas synthesis to be reacted into ammonia. Then, ammonia is reacted with CO_2 into urea product.

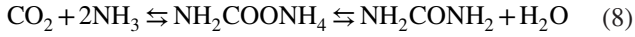
In the process of the combined PV Electrolysis without battery (PV EI) mode, operational hydrogen production during the day is made with combined PV Electrolysis and SR or BG, while at night, the full hydrogen production is supplied from the SR process or BG process.

2.3 | Urea production process

Urea is, in many ways, the most convenient form for fixed nitrogen. It has the highest nitrogen content available in a solid fertilizer (46%). It is easy to produce as prills or granules and is easily transported in bulk or bags with no explosive hazard. It leaves no salt residue after use on crops. Its specific gravity is 1.335, decomposes on boiling, and is fairly soluble in water. Urea is an organic compound composed of elements of carbon, hydrogen, oxygen, and nitrogen by the formula CON_2H_4 or $\text{CO}(\text{NH}_2)_2$. Urea is also known as carbamide, which is mainly used in Europe. Other names that are also often used are carbamide resin, isourea, carbonyldiamine, and carbonyldiamine. This compound is the first synthetic organic compound to be successfully made from inorganic compounds. In addition to the soil fertilizer, the utilization of urea products in everyday life is also quite extensive, either in the form of derivative products or direct use.

The raw materials of urea products are ammonia (NH_3) and carbon dioxide (CO_2), which are the products of the ammonia plant from the CO_2 removal unit at the ammonia plant.

Here is a description of the reaction process of making urea with NH₃ and CO₂ raw materials.¹⁸



In the manufacturing of urea products, the production process is divided into four units: synthesis unit, recirculation unit, evaporation and finishing unit, and waste water treatment unit.

3 | METHODOLOGY

3.1 | Green urea concept

Figure 2 illustrates hydrogen generation from biomass gasification and PV electrolysis for green urea production. The nitrogen raw material is obtained from the air separation unit by separating nitrogen and oxygen in a cryogenic process, and CO₂ is derived from the ammonia plant byproduct or from the flue gas of power plant.

Nitrogen and hydrogen are reacted in an ammonia converter, forming ammonia. The ammonia is then reacted with the CO₂ from the urea plant to form a green urea product.

3.2 | Simulation of production green urea

As design basis, the capacity of urea plant is 569 250 MT/year. For hydrogen production, the feedstock of biomass gasification is empty fruit bunch of palm oil, whereas the SMR process uses natural gas, and PV Electrolysis uses

solar energy. The steady state mass and energy balance of each process in the manufacturing of green urea from different process paths are performed using Aspen Plus.^{19,20} The simulation process of hydrogen production through biomass gasification and PV electrolysis are shown in Figures 3 and 4, whereas the simulation process flow diagram of SMR and ammonia synthesis, and urea production are presented in Figures 5 and 6.

In the first stage, the ammonia production simulation consists of several units: desulfurization unit, reforming unit, carbon monoxide conversion unit, carbon dioxide removal unit, methanation unit, ammonia synthesis unit, and refrigeration unit. After ammonia is formed, it is followed by urea plant simulation including urea synthesis units, recirculation units, and evaporation units. The CO₂ source, especially for PV electrolysis, comes from flue gas of coal-based power plant. The flue gas needs to undergo water removal process using separator vessel before use. CO₂ treatment is located in ammonia plant. The CO₂ compression is integrated in urea plant.

Gasification process is simulated using combined steam-air as gasifying agent with all reactions and the kinetics data are taken from study of Pauls et al.²¹ For PEM electrolyzer is assumed with performances of 57%-64% LHV or 58-52 kWh of electricity per kg of H₂.²²

By using electricity consumption data from the PV electrolysis process, the capacities of photovoltaic-based power plant and the battery necessary can be obtained. The PV power plant capacity factor is assumed to be 20%-25% and

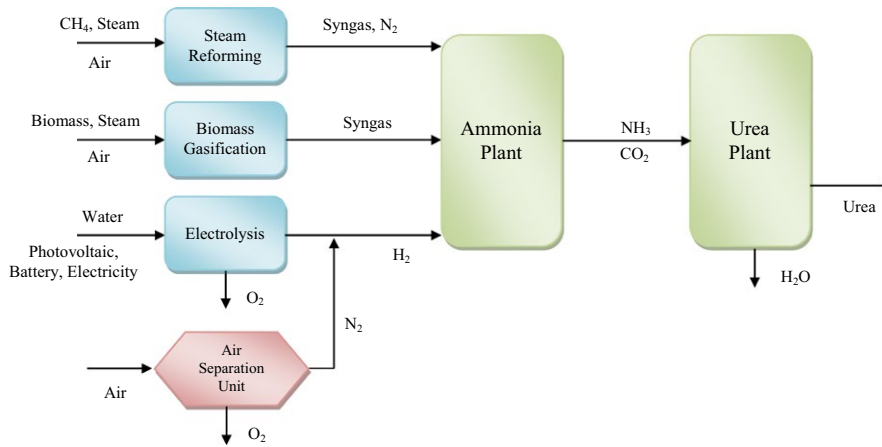


FIGURE 1 Block flow diagram green urea production

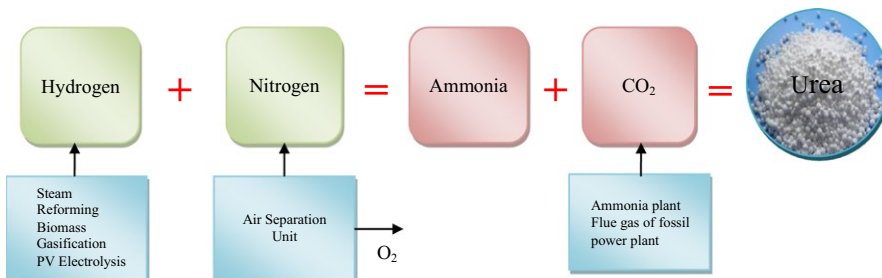


FIGURE 2 Renewable energy-to-urea concept

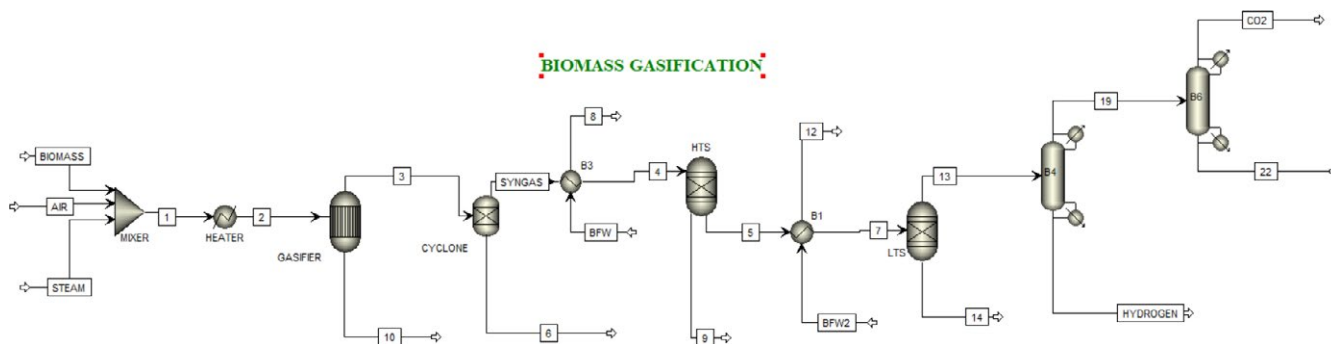


FIGURE 3 Biomass gasification flow sheet

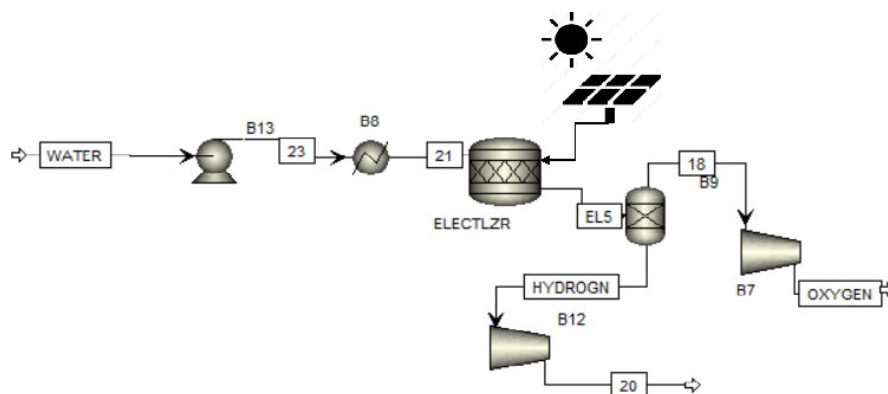


FIGURE 4 Photovoltaic electrolysis flow sheet

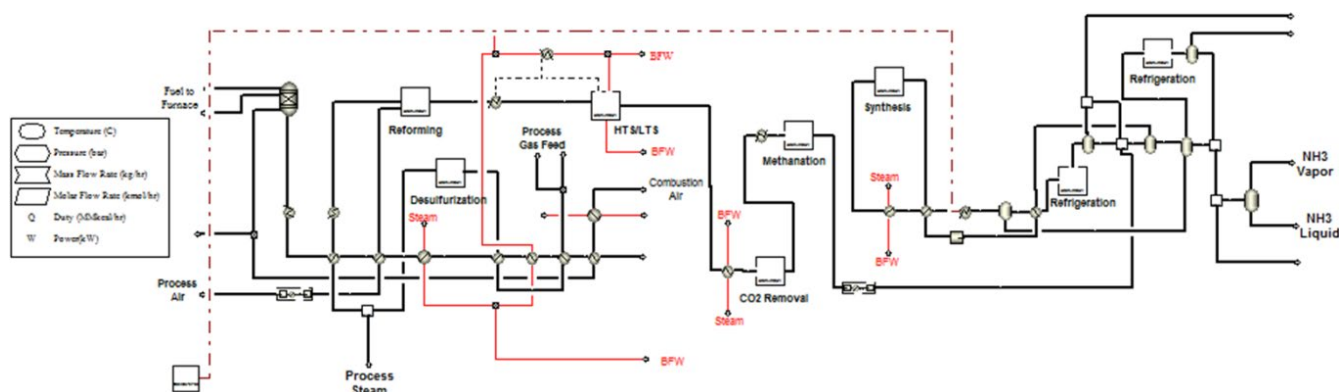


FIGURE 5 Flow sheet steam methane reforming and ammonia synthesis

the electricity loss during the charging-discharging of the battery and the electrolysis process is 5%.²³ Commercially crystalline silicon (c-Si) solar cells used in this study with efficiency of around 21%-23%.¹⁷ Yearly average of solar irradiation in East Borneo island is assumed 1706 kWh/m² and yearly average PV power potential is 1323 kWh/kWp.¹⁶ The battery used is lithium-ion type with current density between 200 and 735 Wh/L and round-trip efficiency of 92%-96%.²³

By converting raw materials and using the steam reforming process, the biomass gasification process, PV electrolysis process, and the combination of the three processes technical data covering raw material consumption, H₂O consumption, electricity consumption, H₂/CO₂ ratio, CO₂ emissions, and total green urea product will be produced.

3.3 | Optimization model

All stages involved in the simulation and optimization processes are displayed in the diagram in Figure 7.

3.3.1 | Production cost projection

Production cost is calculated based on a levelized cost method consisting of capital expenditures (Capex), fixed operating and maintenance costs (O&M), and feedstock. The details of the production cost components of each technology from 2020 to 2050 are given in Table 1:

Capex is the money a company spends to invest its fixed assets. O&M is a variable cost for operation and maintenance

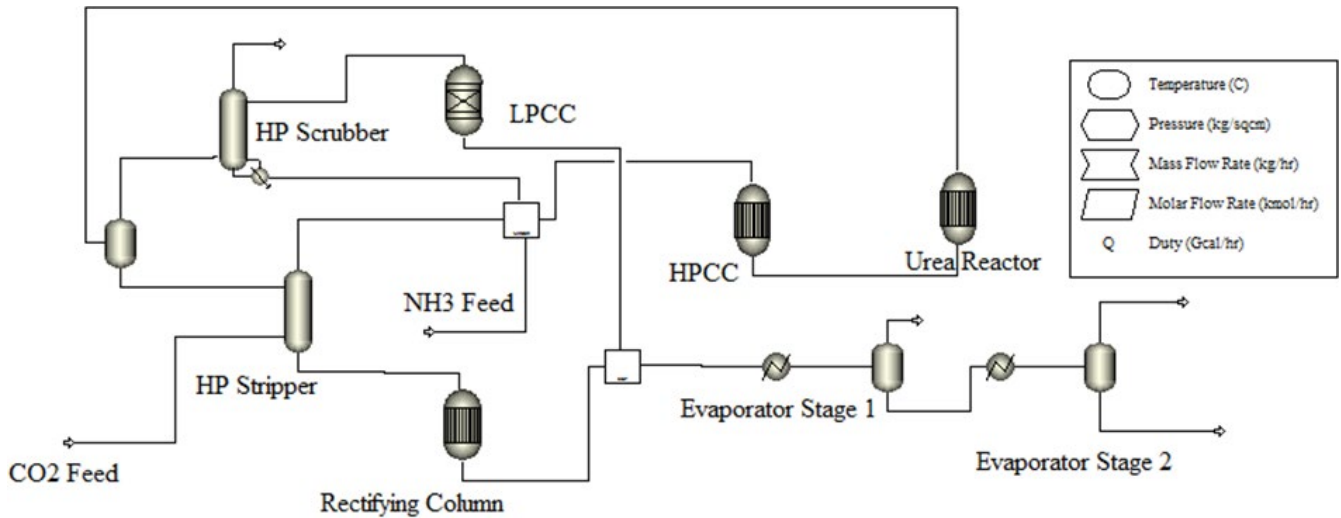


FIGURE 6 Urea synthesis flow sheet

activities; the value of O&M is typically about 10%-20% of Capex.²⁴ Feedstock is a variable cost for the purchase of raw materials.

3.3.2 | Minimization of urea production cost

The first objective function is to minimize the total cost of producing urea (OF1). The average urea production cost is used to calculate OF1, influenced by several cost factors: capital expenditure (C), operating and maintenance costs (O), and feedstock costs (F), among others.

Equations for the production cost objective function can be written as:

$$OF1 = \sum_{t=1}^T \sum_{i=1}^I (1+r)^{-t} (q_{it} TPC_{it}) \quad (9)$$

$$TPC_{it} = (C_{it} + O_{it} + F_{it}) \quad (10)$$

where r is the discounted rate, t is the year, T is the lifetime of plants, q is the urea produced by each hydrogen technology, i is the type of hydrogen production technology as a decision variable in the model, and TPC is total production cost. The calculation is based on a bank interest assumption of 5%, inflation rate of 4%, plant lifetime about 30 years,²⁴ and a period from 2020 to 2050.

The projected capital expenditure for each hydrogen production technology as a parameter in Equation 9 is based on the learning curve model, which results in a relationship between the cumulative installed capacity and future capital expenditures.²⁵ With the projected cumulative installed capacity, capital expenditures can be estimated by:

$$C_t = C_0 N_t^\phi \quad (11)$$

where $1 - 2^\phi$ is the technology learning rate, which is defined as the percentage reduction in future capital expenditure C_t for

every doubling of the cumulative capacity (N_t). The value 2^ϕ is called the progress ratio as a measure of the speed of learning, and C_0 is the capital expenditure in the basis year (2017). The progress ratio is 82% for electrolysis technology, 89% for steam reforming, and 107% for coal gasification.²⁵

3.3.3 | Minimization of CO₂ emissions

The second objective function is to minimize the total CO₂ emissions (OF2) over the entire life cycle of urea production technologies. A research developed a model GHG prediction for various ammonia production methods for life cycle assessment (LCA) analysis based on the cradle-to-gate method, starting from the various raw materials used until the formation of urea products.²⁶ CO₂ from flue gas is considered as a deduction from CO₂ emission. A cradle-to-gate LCA study was carried out with MS Excel. The system boundary of LCA is from the LCI data that were extracted from the ASPEN Plus flow sheets and some LCI data of feedstocks taken from previously described.^{22,27,28} The flow sheet is divided into three main processes (hydrogen production and utilities plant, ammonia plant, and urea plant). The CO₂ life cycle emissions are calculated by the coefficient of emission (E) multiplied by the total urea production from each technology, which is given by:

$$OF2 = \sum_{t=1}^T \sum_{i=1}^I E_{it} q_{it} \quad (12)$$

3.3.4 | Urea production capacity constraint

The total urea production from all types of hydrogen technology should be below the total urea plant capacity for a year:

$$\sum_{i=1}^I q_{it} \leq 569\,250 \quad (13)$$

where 569 250 MT/year is the urea plant capacity for a year t .

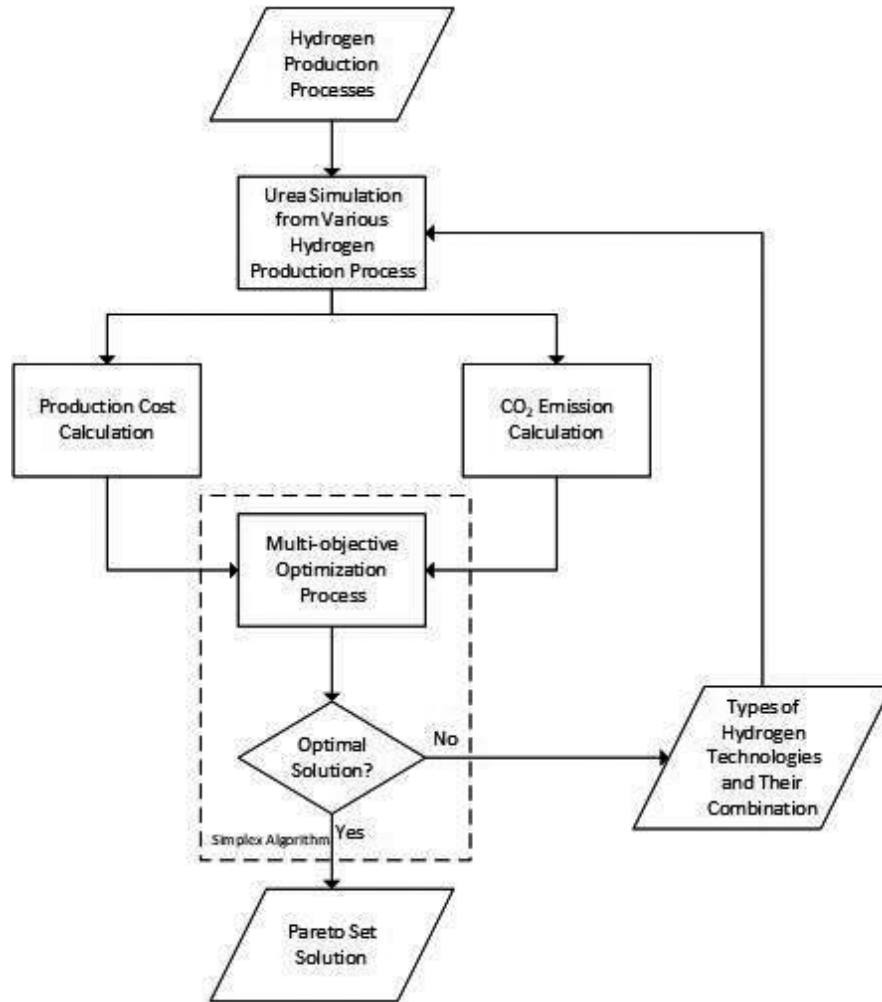


FIGURE 7 Research flow diagram

3.3.5 | H_2/CO_2 constraint

To produce urea, the stoichiometry calculation requires an H_2/CO_2 ratio equal to 3, so for each technology, the hydrogen to carbon dioxide ratio H_2/CO_2 is limited to a range of 2-4. The ratio of H_2/CO_2 for each process is obtained from the mass balance simulation:

$$2 \leq \frac{H_2}{CO_2} \leq 4. \quad (14)$$

3.3.6 | Optimization solution

Optimization model consist of two objective functions as dependent variables. The first one is minimizing production cost and the second one is minimizing CO_2 emission. Decision variables include three types of hydrogen production technologies: steam reforming, biomass gasification, and PV electrolysis and the combination of these technologies. The Pareto curve solution is used to find the best technology or combined technologies to fulfill the multi-objective functions. MOO solution is conducted using ϵ -constraint

method carried out by GAMS software using Simplex algorithm. Optimization will be calculated for every 5 years over 30 year's periods.

4 | RESULTS AND DISCUSSION

4.1 | Production cost

The production cost consists of three main components, namely capital expenditure (Capex), operating and maintenance (O&M), and feedstock. Each process technology has a different cost composition. The breakdown of these costs for each process in each decade from 2020 to 2050 is shown in Figure 8.

The steam reforming process is dominated more by the feedstock cost component than the Capex or O&M cost, so the steam reforming process is very vulnerable to natural gas price changes, which increase every year. The biomass gasification process is dominated by the capex and feedstock costs, but biomass price increases are not expected to be significant in the future, so the total production cost of biomass gasification process is still lower than the

TABLE 1 Cost projection for each process

Parameter	Year						
	2020	2025	2030	2035	2040	2045	2050
Steam reforming							
A. Capex (M USD)	33.3	38.2	43.8	50.3	57.7	66.6	76.0
B. O&M (M USD)	6.7	7.6	8.8	10.1	11.5	13.3	15.2
C. Feedstock (M USD)	90.2	103.5	124.8	149.1	178.5	214.1	257.2
Biomass gasification							
A. Capex (M USD)	65.0	79.1	96.2	117.1	142.4	173.3	210.8
B. O&M (M USD)	19.5	23.7	28.9	35.1	42.7	52.0	63.2
C. Feedstock (M USD)	42.7	44.1	45.6	47.1	48.7	50.4	52.1
PV electrolysis							
A. Capex (M USD)	155.9	172.1	189.2	208.9	229.7	253.6	278.8
B. O&M (M USD)	15.6	17.2	18.9	20.9	23.0	25.4	27.9
C. Feedstock (M USD)	2.5	2.8	3.1	3.4	3.8	4.2	4.6
NG price (USD/MMBTU)	5.6	6.52	8	9.69	11.73	14.20	17.19
Biomass price (USD/MT)	65.83	68.51	71.29	74.19	77.20	80.34	83.61
Urea price (USD/MT)	236	266	300	347.78	403.17	467.39	541.83

steam reforming process. The PV Electrolysis process is dominated by the Capex cost component; the Capex PV Electrolysis cost becomes very high because it requires a battery investment so that the electrolysis process can last for 24 hours, and the urea plant is not shutdown. However, PV Electrolysis has a very fast learning curve so that in the next few years, the value of PV Electrolysis Capex will decrease significantly.

Of the three main processes and the three combined processes, the combined SR-PV El process has the lowest production cost value at 358.8 USD/MT. This is due to the cost component being dominated by the feedstock cost, so that the increase in natural gas price will be compensated by the low cost in PV El raw materials, such that it will not have a significant impact on total production cost.

The comparison of investment value, that is, capital expenditure, of each process is shown in Figure 8. The technology that has the lowest Capex value is the steam reforming process, while the highest is the PV Electrolysis process. This is due to the fact that steam reforming technology is a technology that has long been developed and has matured, while the PV Electrolysis technology is still relatively new, not very mature, and still being developed. So, for the future, the predicted value of Capex PV Electrolysis is lower because of the learning rate. The combined process has a lower Capex value than PV Electrolysis, because it is a combination of investment from both processes.

The value of O&M depends on the Capex value of a process—the higher the Capex value, the higher the O&M value will be. The average value of O&M is in the range of 10%–20% of the value of Capex. The gasification biomass process

requires the highest O&M cost, because the gasification biomass process requires a high enough Capex value, and the material that is handled is a solid base, requiring more manpower and maintenance costs. Unlike the PV El process, although the cost of Capex is very high, the cost of O&M is quite low because the material that is handled is a liquid base, so it does not require very high maintenance costs.

Feedstock cost is strongly influenced by the price of raw materials from a process; the higher the price of raw materials needed, the higher the cost of feedstock. The SR process is dominated by the feedstock cost, accounting for almost 70% of the total production cost, causing the SR process to be very susceptible to natural gas price increases in the future. This is in contrast to the biomass gasification process, which has a low feedstock cost, so the increase of biomass price has no significant effect on total production cost. Likewise, the PV El process has a very low feedstock cost. The comparison of feedstock price is presented in Figure 9.

The increase in production cost of urea manufacturing from each process every year can be seen in Figure 10. Of the eight processes, the PV Elb process is the process that has experienced the lowest increase in production costs from year to year, while the process that has experienced the highest increase in production costs is the steam reforming process. This is because in the steam reforming process, the main component of production costs is the feedstock cost, so the steam reforming process is highly vulnerable to changes in natural gas prices in the future. By combining the SR process with PV El, the feedstock cost can be reduced by 20% because the raw materials used in the PV El process are very cheap.

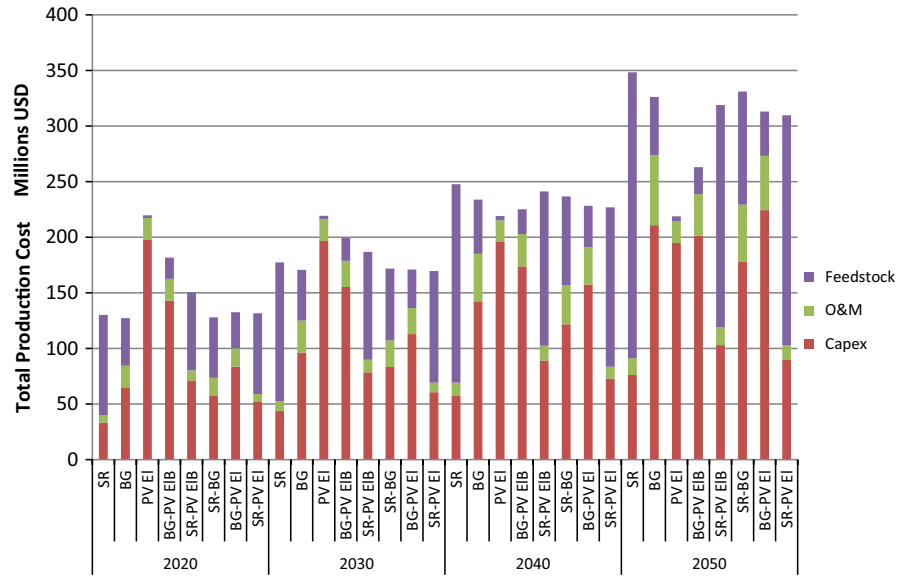


FIGURE 8 Production cost breakdown

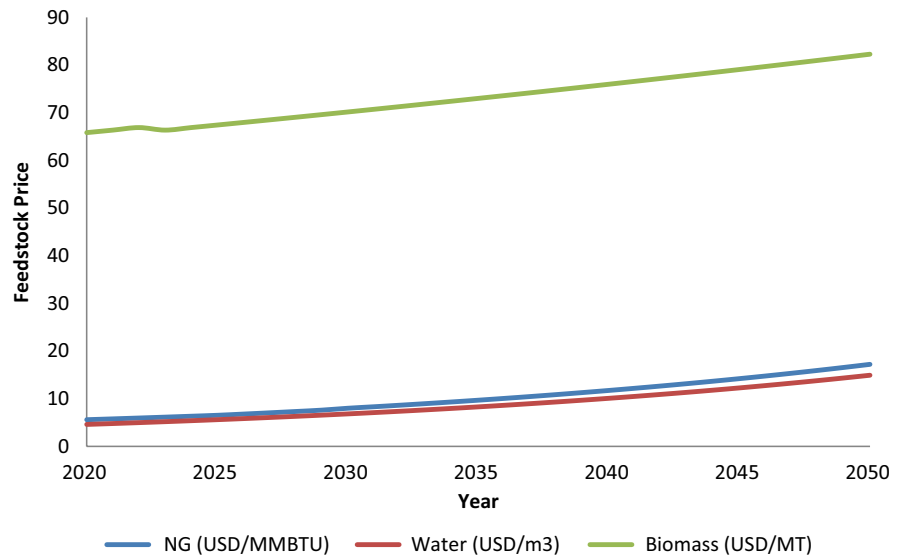


FIGURE 9 Feedstock price comparison

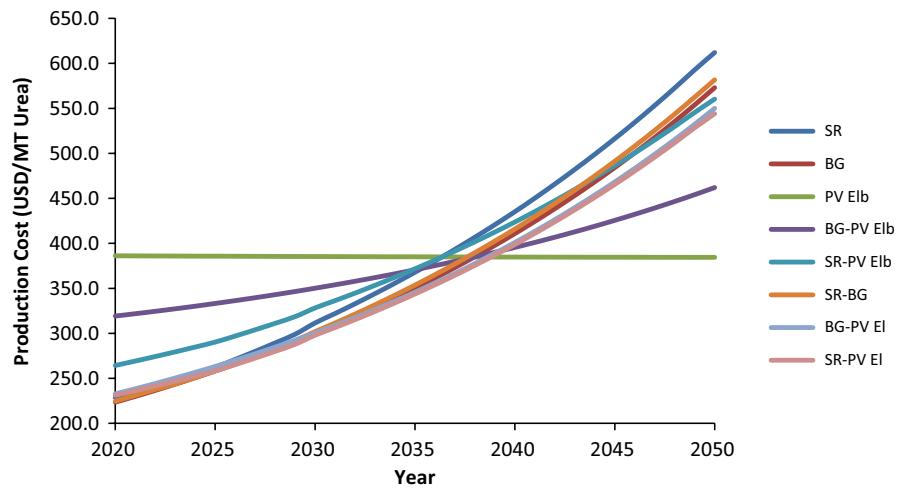


FIGURE 10 Production cost projection

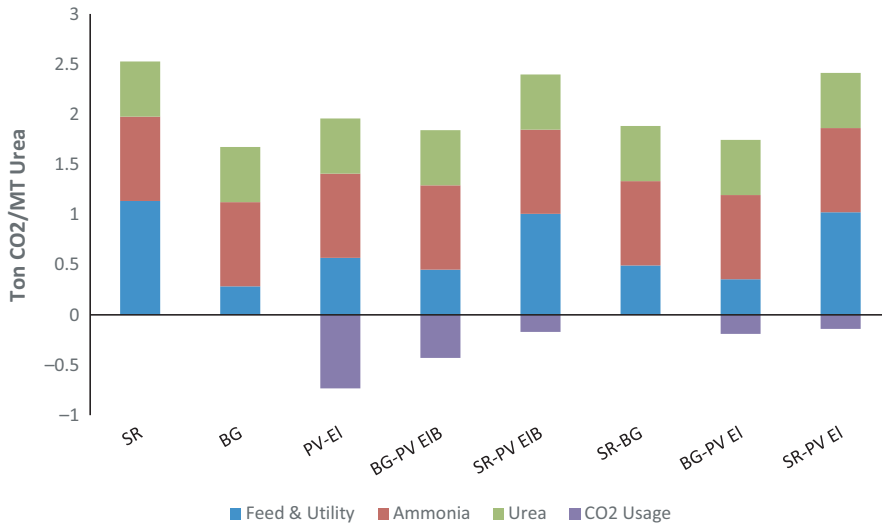


FIGURE 11 CO₂ emission by technology

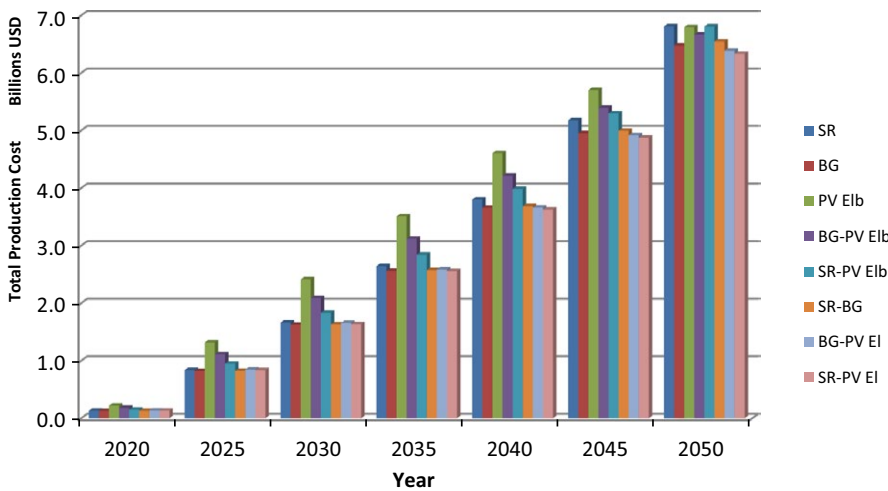


FIGURE 12 Total production cost accumulation

The advantages of combining steam reforming and electrolysis processes are using renewable energy such that the resulting H₂/CO₂ ratio can be adjusted to ~3 according to stoichiometry calculations.

4.2 | CO₂ emission

The goal of the study was to identify the environmental processes in the life cycle of urea production from a renewable feedstock via the biomass gasification and water electrolysis route. The total CO₂ emissions from the least cost optimization results, based on LCA calculations of the renewable energy-to-urea process with the cradle-to-gate method, are shown in Figure 11.

The lowest CO₂ emission for urea synthesis comes from PV Electrolysis without battery, which account for 1.23 ton of CO₂/MT urea, followed by biomass gasification and SMR. This is because the PV Electrolysis uses CO₂ as its feedstock. Thus, there is a reduction in CO₂ emission for every technology that uses PV Electrolysis. Steam methane reforming produces the highest CO₂ emission because it uses fossil-based feedstock. For combined technologies, BG-PV Electrolysis without battery gives

the lowest CO₂ emission which account for 1.56 ton of CO₂/MT urea. This is because these technologies use renewable energy sources, that is solar energy resources for PV Electrolysis and empty fruit bunch of palm oil for biomass gasification.

With reference to the above data, there is a great potential for decreasing CO₂ emissions in the urea industry, which currently still uses the steam reforming process for 740 025 tons/year or about a 51% reduction of CO₂ emission if switched to or combined with PV Electrolysis technology. So, the environmental aspect will be very important in preventing global warming due to buildup of CO₂ in the Earth's atmosphere.

4.3 | Optimization result

Simulations and optimizations were generated for 2020-2050, resulting in a production cost graph shown in Figure 12, a CO₂ emission graph shown in Figure 13, and a Pareto curve shown in Figure 14.

Figure 12 shows the accumulated total production cost from 2020 to 2050, considering the future value of money and the value of the learning curve for each technology. Figure 12

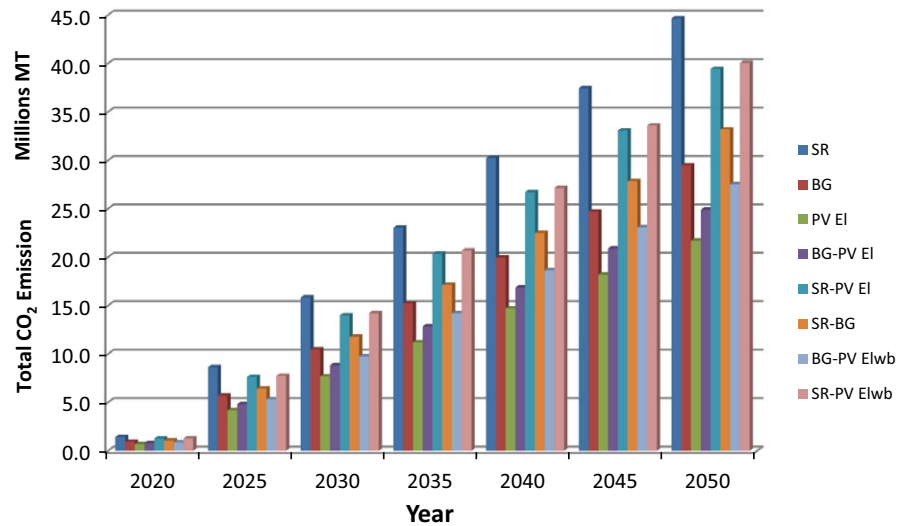


FIGURE 13 Total CO₂ emission accumulation

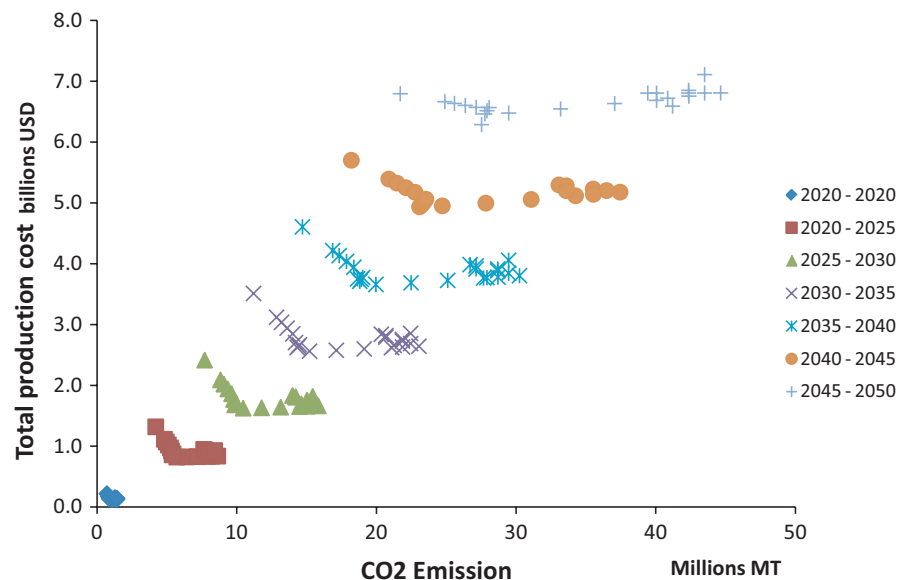


FIGURE 14 Pareto curve

shows that the current state of steam reforming technology is still the cheapest compared to other processes, but in the next few years, the total production cost of the combined SR-PV EI process will be the cheapest in producing urea. This is because the value of the declining PV Electrolysis investment price in the future will decrease significantly with a progress ratio of 82% (according to the data from the learning curve). With a considerable decrease in Capex, the PV Electrolysis technology is predicted to replace the steam reforming process in the future.

The total accumulated CO₂ emissions from each process and the hydrogen production combination processes are shown in Figure 13, with the PV electrolysis process resulting in the lowest accumulation of CO₂ emissions and the steam reforming process producing the highest CO₂ emission accumulation. This is in accordance with the LCA calculations for each process in which renewable-energy-based processes will result in

much lower CO₂ emissions. Reducing CO₂ emissions in the urea industry can be done with a combination of process, such as combining the methane steam reforming process with the PV electrolysis process or with the biomass gasification process.

The goal of MOO is to find the best technologies configuration that can satisfy the objectives. The optimum solution set obtained by Simplex algorithm is the biomass gasification technology from 2020 to 2035 and combined BG-PV EI processes (41% BG, 59% PV EI) from 2040 to 2050, which produce the minimum CO₂ emissions and minimum production costs. The detailed set of MOO solutions is shown by the Pareto frontier, shown in Figure 14.

From 2020 to 2035, technology that produces the lowest production cost and CO₂ emissions is biomass gasification. However, as the capital expenditure of PV Electrolysis decreases throughout time, with a progress ratio of 82%, by the year of 2040, the combined technology BG-PV EI becomes the most optimal with a total production cost of 4916 million

TABLE 2 Mass and energy balance

Material streams	BG-PV EI	BG	PV EI	SR
Process ratio (%)	41/59	100	100	100
Feeds				
Biomass (kg/h)	27 519	66 862	0	0
Natural gas (kg/h)	0	0	0	14 162
Air (kg/h)	21 190	51 485	0	72 978
Steam (kg/h)	34 097	55 000	0	67 000
Water (kg/h)	26 335	0	64 232	0
Intermediates				
Syngas (kg/h)	86 250	86 250	86 250	86 250
H ₂ (kg/h)	7188	7188	7188	7188
N ₂ (kg/h)	33 541	33 541	33 541	33 541
CO ₂ (kg/h)	48 086	81 501	0	51 125
Ammonia (kg/h)	40 729	40 729	40 729	40 729
Products				
Urea (kg/h)	71 875	71 875	71 875	71 875
Electricity consumption (kW)	203 152	27 559	325 977	13 420
CO ₂ excess/consumption (kg/h)	−7242	28 792	−52 708	−1583
CO ₂ emissions (ton CO ₂ /MT urea)	1.41	1.67	1.23	2.53

USD and CO₂ emissions equal to 23 million tons of CO₂. Meanwhile, the Combine SR-PV EI technology experiences a significant decrease in production cost by 2040, but its CO₂ emissions are still high due to the SR technology based on fossil raw materials.

In the steam reforming process, the CO₂ emission value is high because it uses a methane, and the value of the production cost will be high enough in the future. Thus, steam reforming process is much less optimal compared to the PV Electrolysis process and biomass gasification.

Figure 14 shows that biomass gasification and the combined technology BG-PV EI exhibit a technological breakthrough in reducing production cost and CO₂ emission in the urea industry, replacing steam reforming technology, which is still based on fossil fuels and susceptible to increases in the price of natural gas. For short-term alternatives, the combined SR-PV EI technology can be used to reduce production cost and CO₂ emissions in the urea industry.

The mass and energy balance of optimal solution and its comparison with each technology is presented in Table 2.

5 | CONCLUSION

This paper presents a multi-objective approach for optimizing a green urea production strategy to minimize the production costs and environmental impacts by considering the future cost

development of technology and feedstock price for each technology in the time frame of 2020–2050. The primary analysis was focused on the economic and environmental concerns in supporting future urea demand until 2050. The MOO reveals some optimal solutions for more sustainable green urea production in the future, providing support for decision makers to balance production costs and CO₂ emissions. The best solution is to minimize green urea production costs while considering environmental aspects by increasing the role of renewable energies.

From the eight processes of optimized hydrogen production technology using MOO methods, the best process that meets the economic and environmental aspects to replace the steam reforming process in the future is the biomass gasification process from 2020 to 2035 and the combined biomass gasification (41%)—PV electrolysis without battery (59%) process, which is based on renewable energy, from 2040 to 2050.

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