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RESEARCH ARTICLE

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# LCA comparison analysis for two types of $H_2$ carriers: Methanol and ammonia

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**Summary**

This paper presents a comparative life cycle assessment of two types of $H_2$ carriers, methanol and ammonia, using GaBi 10 software. Two types of $H_2$ carriers that is, methanol and ammonia are compared from coal, natural gas and renewables, respectively. The full supply chain is considered in the carbon footprint evaluation, which contains production, storage, transportation, and utilization phase. The energy analysis results show that $H_2$ carrier produced from natural gas has higher energy efficiency than that from renewables, which can be attributed to the high energy consumption during $H_2$ generation in the latter. Carbon footprint evaluation indicates that solar PV-based ammonia production route has the lowest GWP in all scenarios, with a value of 43.9 g of $CO_2$-Equation $MJ^{-1}$ of ammonia. In addition, electricity has been found as the key factor affecting GHG emissions in the routes of fuels produced from renewable $H_2$ through sensitivity analysis. By optimizing electricity generation and expanding the carbon capture scale of power plant, the GHG emissions level of CCU-based methanol production route and solar PV-based ammonia production route can be further reduced.

**KEYWORDS**

ammonia, carbon footprint, hydrogen carrier, life cycle assessment, methanol

## 1 | INTRODUCTION

By the end of 2020, the concentration of atmospheric $CO_2$ has risen from 280 ppm before the start of the Industrial Revolution (mid-1700s) to 412.5 ppm.[1] Climate change has become a major crisis and challenge faced by all countries in the world and more than 190 countries have signed the Paris Agreement, whose goal is "to limit global warming to well below 2, preferably to 1.5 degrees Celsius, compared to pre-industrial levels."[2] To meet this long-term temperature goal, extensive effort should be paid for reducing greenhouse gas (GHG) emissions. Considering that a large portion of $CO_2$ emissions is derived from the usage of fossil fuels, gradually replacing of fossil fuels with alternative fuels in power and energy system is a promising solution for decarbonization. In this regard, $H_2$ is considered as potential enables of zero-carbon society in the future. However, due to the low volume energy density and difficulties for storage of $H_2$, methanol, and ammonia are suggested as a good chemical bond solution for $H_2$.

Methanol, $CH_3OH$, is the simplest alcohol with gravimetric hydrogen density of 12.5%, which can be used as a good $H_2$ carrier. Besides, methanol is also regarded as a potential transport fuel due to its scalability. Verhelst et al.[3] reviewed the performance of methanol applied to combustion engine, mainly focus on the use of methanol as a pure fuel or blend component for internal combustion engine. Because of a series of excellent properties, methanol engine has obvious advantages over gasoline engine in terms of peak efficiency and emission performance.[3,4] Generally, methanol is produced through syngas, which consists mainly of $H_2$ and CO. Conventional methanol production process emits a considerable amount of pollutants, such as $NO_x$, $SO_2$ as well as $CO_2$. From this point, there are many previous studies associated with the environmental evaluation of methanol production in the recently. Li, C. et al.[5] evaluated the environmental impacts of two coal-based methanol production routes in China, concluding that comprehensive performance of methanol production by coal coking technology is better than that by coal gasification technology, especially in terms of global warming. Liu et al.[6] established the process models of coal-to-methanol and biomass-to-methanol and studied the environmental impacts and energy consumption of the two production methods via the process simulation. In order to alleviate the burden of large GHG emissions from traditional methanol production, people try to develop renewable methanol production routes, of which the most concerned is through the hydrogenation of carbon dioxide.[7] Based on the regional characteristics of Japan, Morimoto et al.[8] estimated the efficiency and environmental performance of carbon capture utilization (CCU)-based methanol production through process simulation and determined the optimal implementation scheme of CCU technology from the perspective of $CO_2$ emission reduction.

Ammonia, $NH_3$, is an attractive hydrogen carrier due to its highest hydrogen mass density 17.6%. Since ammonia does not contain carbon, the application of ammonia as a clean fuel in the combustion field has received attention internationally recently. Studies have proven that ammonia can be effectively used in engines, boilers, and gas turbines.[9-11] The typical ammonia production process, known as Haber-Bosch process, converts $H_2$ and $N_2$ into $NH_3$ at high temperature (350°C-550°C) and high pressure (10-25 MPa) in the present of an iron-based catalyst.[12] However, conventional ammonia synthesis is an energy-intensive process, and it is estimated that about 420 million tonnes of $CO_2$ emission come from worldwide ammonia plant, accounting for over 1% of the total energy-related $CO_2$ emissions.[13] Bicer et al.[14] conducted a comparative study on conventional resource-based ammonia production via a comprehensive life cycle assessment. There are many existing studies that focus on improving the environmental performance of ammonia production by optimizing its processes, especially in the terms of global warming. Chisalita et al.[13] investigated an environmental assessment of ammonia synthesis through conventional and green hydrogen production routes. The result shows the GHG emissions burden can be significantly reduced by implementing Chemical Looping Hydrogen production technology instead of Steam Methane Reforming. Karaca et al.[15] reported carbon footprint of different nuclear-based ammonia synthesis options by means of the life cycle assessment tool, the global warming potential (GWP) results ranging from 0.18 to 0.337 t $CO_2$-eq/t $NH_3$.

It is worth noting that, for the two $H_2$ carriers studied in present work, most of previous literatures were focus on the environmental impact assessment of upstream production phase, while the life cycle assessment of the full supply chain including production, transportation, and utilization phases were rarely reported. In addition, comparative studies on the environmental performance of the entire supply chain of different $H_2$ carriers remains limited, and there are still some open questions that need further understanding, regarding to which factors profoundly influence the difference in GHG emission levels of two $H_2$ carriers as well as how much the mitigation potential is for two $H_2$ carriers respectively if the key factors are improved. Thus, in the present study, a "cradle-to-grave" life cycle assessment is used to evaluate and compare carbon footprint of two $H_2$ carriers considering various production routes. Total GHG emissions from fuel production, land storage, long-distance rail transportation, and utilization of methanol and ammonia are considered in this work. As the factors that affect the GHG emissions emitted from $H_2$ carriers supply chain vary from region to region, regional characteristics should be considered when implementing comparative studies. This work is based on the nation conditions of China. The purpose of this work is to provide reliable and effective data basis for the future application of alternatives in energy systems, which can offer a certain degree of guidance for future planning and policies making.

## 2 | METHODOLOGY

### 2.1 | Life cycle assessment method

LCA is a methodology used to evaluate the environmental impact of a product throughout its life cycle, from the acquisition of raw materials, product manufacturing to use until the final disposal.[16] To standardize the implementation of LCA, the International Standards Organization constituted a methodological framework for conducting LCA, which includes four steps namely goal and scope definition, life cycle inventory (LCI) analysis, life cycle impact assessment (LCIA), and interpretation.

### 2.2 | Goal

This study aims to compare the comprehensive environmental performance of two carbon-free or carbon-neutral $H_2$ carriers produced from coal, natural gas or renewable resource in their own supply chain. We focus on the total amount of greenhouse gases emitted throughout their whole supply chain, from raw materials acquisition and processing, liquefied energy carrier production and storage to the transportation until end-use of product. According to the different sources of raw materials and

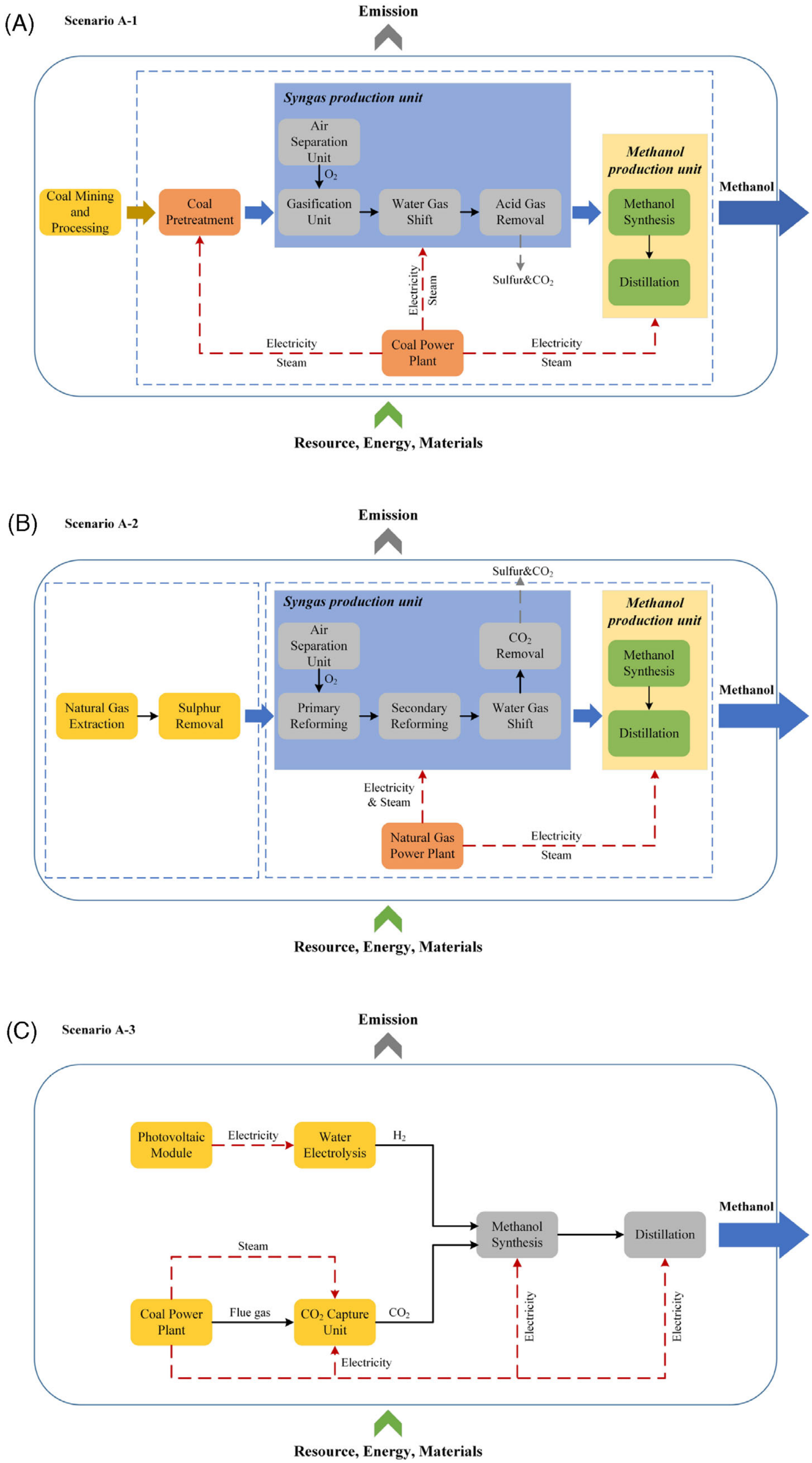



**FIGURE 1** The schematic system diagram of A, Coal-$CH_3OH$ route, B, NG-$CH_3OH$ route, C, PV/CCU-$CH_3OH$ route

final product types, there exist six comparative scenarios in this study: (1) coal-based methanol (Coal-$CH_3OH$); (2) natural gas-based methanol (NG-$CH_3OH$); (3) PV and carbon capture and utilization (CCU)-based methanol (PV/CCU-$CH_3OH$); (4) coal-based ammonia (Coal-$NH_3$); (5) natural gas-based ammonia (NG-$NH_3$); (6) solar PV-based ammonia (PV-$NH_3$).

#### 2.2.1 | Scenario A-1: Coal-$CH_3OH$

Although various production technologies are different, all the industrial methods for producing methanol from hard coal mainly contain three fundamental stages namely coal mining and processing, syngas production, methanol synthesis, and distillation. As shown in Figure 1A, raw material is mined from the coal mine and sent to a nearby methanol production plant. After pretreatment, the feed coal is put into gasifier along with oxygen produced from air separation unit. In the gasifier, oxygen and steam directly contact with the coal, triggering a series of chemical reactions that eventually produce crude syngas. Crude syngas prepared by coal gasification cannot meet the requirements of methanol manufacture, so water-gas shift reaction (adjust H/C molar ratio to 2.05-2.15) and purification process (remove $CO_2$ and sulfur-containing impurities in the feed gas) are needed. Finally, under the action of copper/zinc-based oxide catalyst,[17] the clean syngas is converted into methanol and refined methanol is obtained by final distillation process.[18]

#### 2.2.2 | Scenario A-2: NG-$CH_3OH$

Unlike the coal-to-methanol technology, manufacturing methanol from natural gas uses steam reforming process to produce syngas. In this work, the two-step reforming process is used because it can give better results for larger methanol synthesis plants.[19] As shown in Figure 1B, natural gas is extracted from ground and sent to a processing factory to be desulfurized. Then, the treated natural gas is converted into syngas through the two-step reforming process which features a combination of fired tubular reforming (primary reforming) followed by oxygen-fired adiabatic reforming (secondary reforming).[20,21] At last, clean syngas is used for methanol synthesis through a heterogeneous gaseous phase catalysis and refined methanol is obtained by final distillation unit.

#### 2.2.3 | Scenario A-3: PV/CCU-$CH_3OH$

The $CO_2$-to-methanol technical route contains three key steps, namely capture of $CO_2$, production of $H_2$ by water electrolysis, and hydrogeneration of $CO_2$ to synthesize methanol. We assume that the $CO_2$ source is exhaust gas from power plant which supplies electricity and steam for system. As shown in Figure 1C, in the carbon capture stage, the flue gas enters the absorber under the drive of the fan. When sufficient $CO_2$ has been absorbed, the solvent is pumped into the regeneration column where $CO_2$ is separated from the absorber under the action of steam. In the $H_2$ generation stage, water electrolysis is used to produce $H_2$, which is powered by photovoltaic. At last, $H_2$ and captured $CO_2$ are sent into the methanol synthesis system where methanol is produced by the catalytic hydrogenation of captured $CO_2$.

#### 2.2.4 | Scenario B-1: Coal-$NH_3$

Producing ammonia from hard coal adopts coal gasification process. As shown in Figure 2A, similar to coal-to-methanol technology, the feed coal is converted to syngas in the presence of oxygen and steam in the gasifier. In addition to producing oxygen, the air separation unit also separates nitrogen from air for subsequent gas purification and synthesis of ammonia. After gasification, crude syngas needs to pass through water gas shift unit and purification unit, and then treated syngas is fed into ammonia synthesis unit to produce synthetic ammonia. Crude synthetic ammonia still needs further purification to obtain the target product.[22]

#### 2.2.5 | Scenario B-2: NG-$NH_3$

In the natural gas-to-ammonia technology, steam reforming process is used to produce ammonia. As shown in Figure 2B, the feed gas removes the sulfur components in the gas through the desulfurization process, and then passes through one-stage conversion and two-stage conversion to generate crude syngas. After CO high-temperature conversion, low-temperature conversion, $CO_2$ removal and other processes, the crude syngas is converted into a mixture of $N_2$ and $H_2$, which is the main feedstock for ammonia synthesis. Then, the molar ratio of $N_2$ to $H_2$ in the syngas is adjusted to 3. Finally, the treated syngas is pressurized by the synthesis gas compressors and enters the ammonia synthesis system to produce ammonia.

#### 2.2.6 | Scenario B-3: PV-$NH_3$

Electrolysis-based ammonia manufacture technology combines water electrolysis for hydrogen production and the Haber-Bosch process for ammonia synthesis. In this

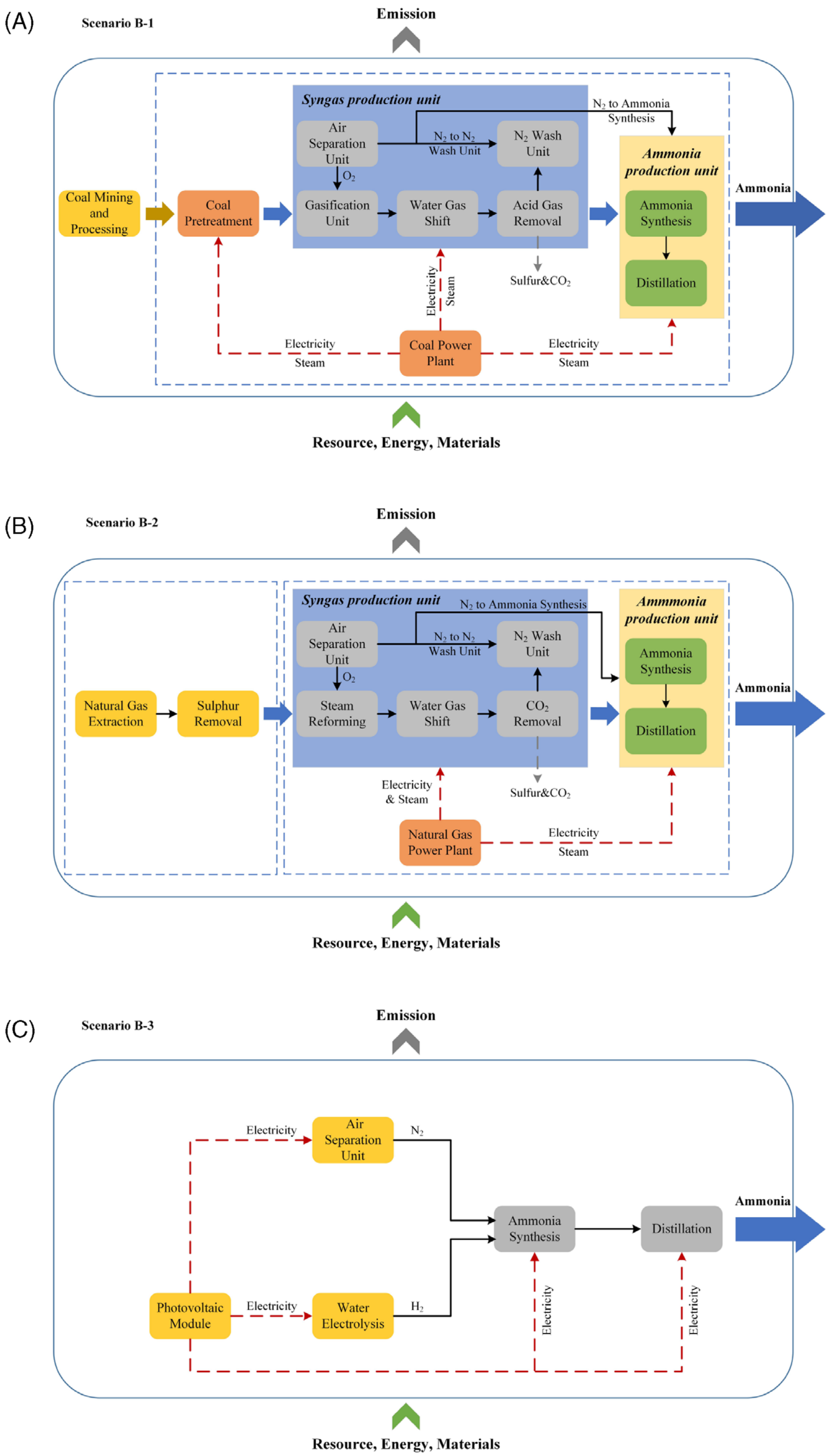



**FIGURE 2** The schematic system diagram of A, Coal-$NH_3$ route, B, NG-$NH_3$ route, C, PV-$NH_3$ route

work, we select solar photovoltaic (PV) as the power source for splitting water to produce $H_2$ and $O_2$. Solar PV, which can directly convert solar radiation into electricity, is gradually regarded as a potential alternative to fossil fuels due to its own advantages. The specific process is shown in the Figure 2C.

## 2.3 | System boundary and scope

A flow-process diagram for the $H_2$ carriers supply chain is shown in Figure 3. The "cradle to grave" is defined as the system boundary of all the six comparison scenarios, which covers the material and energy production chain and all processes from the raw material extraction through the production, transportation, and use phase up to the product's end of life treatment.[23] The study assumes that both methanol and ammonia production plants are located in northwest China, where coal, natural gas and solar energy resources are abundant. The transportation and application of methanol and ammonia are considered, as the two $H_2$ carriers emit different amount of GHG into environment during transportation and utilization stage. The transportation stage contains three parts, respectively the land storage, loading, and unloading and railway transport. We choose freight train as the transportation mode, and the transport distance is selected as 1500 km. After arriving at the destination, product is used as fuel in an internal combustion engine in all involved routes. What needs illustration is that the transportation of feedstock and auxiliary materials is excluded from the scope of this study, since the manufacturing plant is a pithead plant in all the cases. This simplified method has also been reported in other literatures.[24,25] All the relevant energy (electricity, heat, etc.) and material (water, catalyst, etc.) consumption and treatment at each stage of supply chain are considered, which adhere to China standards as far as possible. In addition, the GHG emission during infrastructures and facilities construction are contained in the LCA system. However, due to the lack of relevant data, this study does not involve the recycling of materials and the utilization of by-products.

## 2.4 | Functional unit

The functional unit is the quantified definition of the function of a product.[16] So, to compare two $H_2$ carriers, their functional units must be equivalent. In this study, the functional unit is defined as 1 kg and 1 MJ of $H_2$ carrier produced from coal, natural gas, and renewables.

## 2.5 | Life cycle inventory analysis

The second part of LCA is LCI, which involves the compilation and quantification of inputs and outputs for a given system or process.[23] The key step in LCI is life cycle data collection.

### 2.5.1 | Life cycle data of raw material preparation

Life cycle data of coal mining and processing, coal mine construction, and commissioning/decommission are mainly based on the results of Liang et al.[26] The

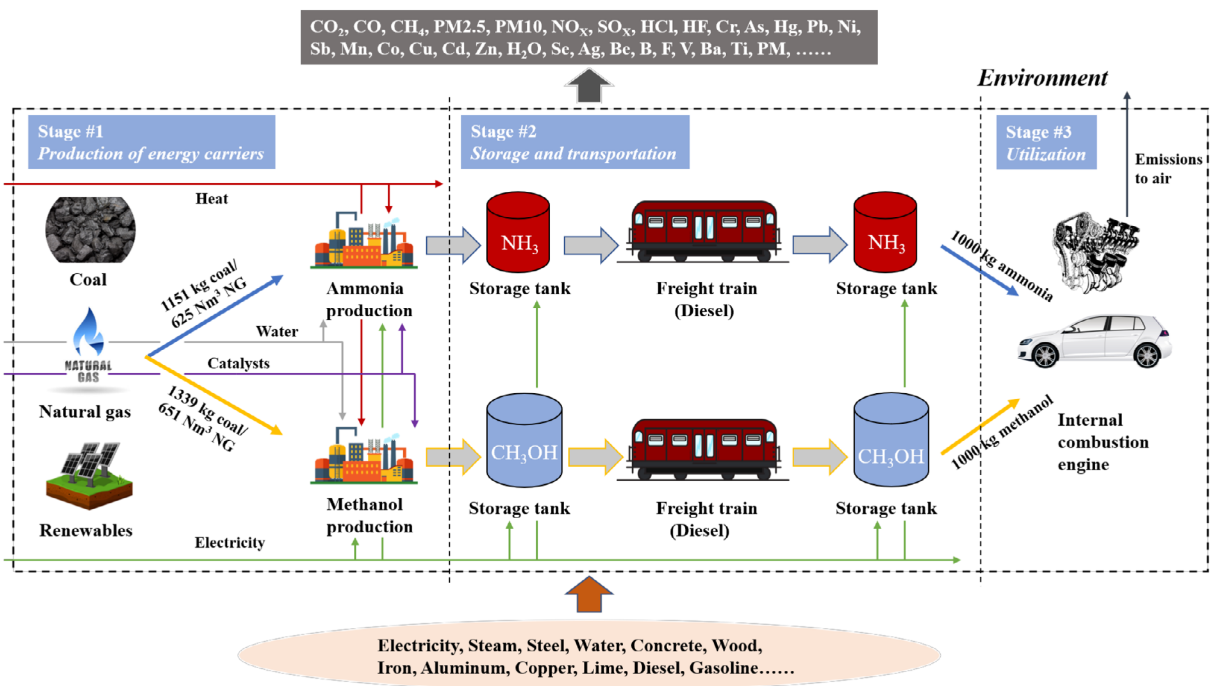



FIGURE 3 Energy carriers supply chain LCA scheme

proximate and ultimate analyses of sample coal are shown in Table S1. Data of natural gas extraction and desulfurization as well as corresponding infrastructure construction are obtained from the typical projects operated in China.[27] Table S2 lists the basic composition of nature gas. Data of construction, operation, and emission of post-combustion carbon capture device are obtained from an industrial-scale $CO_2$ capture plant in China.[28] The operation data of hydrogen production by water electrolysis via PV energy are collected from Spath PL's result.[29] The LCI data of solar PV plant are based on the GaBi database[23] which includes the manufacturing and operation of the system. Liquid nitrogen is produced by the cryogenic separation of air, and the LCI data are also based on GaBi database.[23]

#### 2.5.2 | Life cycle data of onsite methanol production

For coal-based methanol production route, the operation data of coal gasification and methanol synthesis came from Liu's results as well as from modern coal chemical technology books.[30] The manufacturing plant construction data are based on Ecoinvent database.[19] For natural gas-based methanol production route, since methanol production is a highly integrated process, only the efficiency and energy consumption data for the entire process are available, so the syngas production unit is not simulated separately. The LCI data of this technical route are all from Ecoinvent database.[19] For CCU-based methanol production route, the average data are collected from the Ravikumar's research work,[31] which summarizes common 14 scenarios based on literature reviews.

#### 2.5.3 | Life cycle data of onsite ammonia production

For coal-based ammonia production route, the relevant data are from a stable 500 000 ton/year ammonia plant in China, covering the raw material to liquid ammonia products.[32] For natural gas-based ammonia production route, primary data used in this study are collected on fertiliser production for the year 2013 to 2014.[19] These data were based on annual average data based on different production plants in China. For solar PV-based ammonia production route, Bicer et al.[33] concluded that for an ideal Haber-Bosch process, combining 0.177 kg hydrogen with 0.823 kg nitrogen can produce 1 kg ammonia through analyzing electrolysis-based ammonia generation processes.

#### 2.5.4 | Life cycle data of products transportation and utilization

In China, methanol is mainly transported overland freight followed by train.[6] However, there are some issues with road transport mode, such as high cost and great insecurity, and for long-distance transportation, railway has obvious advantages.[34] A similar situation exists for ammonia transportation. For this reason, we choose freight train as the main mode of transportation in this study. Data on energy requirements and operation emissions as well as locomotive construction are taken from the Ecoinvent database.[19] In addition, GHG emissions due to leakage and Boil-Off Gas (BOG) during transportation stage, including land storage, loading and unloading, and railway transport, are also considered in the LCA. The BOG generation rate of energy carriers refers to the research results of Al-Breiki et al.[35] At the last utilization stage, the $H_2$ carrier is consumed as fuel for the internal combustion engine. The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model collects data on combustion and emission characteristics of $H_2$ carriers as vehicle fuels, which were used in this study.[36]

### 2.6 | Life cycle impact assessment

Life cycle impact assessment is a step for identifying and evaluating the potential environmental impact.[37] The so-called CML 2001 method is applied to LCIA calculation, which mainly includes the following impact categories: global warming potential, acidification potential, ozone depletion potential, photochemical ozone creation potential, eutrophication potential, and abiotic depletion potential.[38] In this paper, we focus on the GHG emission of the complete supply chain of two $H_2$ carriers produced in China.

## 3 | RESULTS AND DISCUSSION

### 3.1 | Energy analysis

Energy analysis is a vital method to evaluate energy utilization in the whole life cycle. It performs quantitative analysis of energy input and output in the objective system, so the energy demand, energy conversion, and other processes at different stages as well as the energy efficiency of the whole system can be settled through energy statistics. The production process of energy carrier is the main source of energy consumption in the whole supply chain, so it is necessary to conduct energy analysis at this stage. In this paper, we define a cradle-to-gate energy efficiency to assess the energy utilization performance within different $H_2$ carrier production processes. The cradle-to-gate energy efficiency is defined as follow,

$$\eta = \frac{E_M}{E_{total}}, \quad (1)$$

Where $E_M$ represents the low heating value of the two $H_2$ carrier, $E_{total}$ refers to the total energy consumption in the production stage.

As can be seen from Table 1, from the energy analysis point of view, NG-$CH_3OH$ route has the best performance with net energy efficiency of 60.4% of all scenarios, followed by NG-$NH_3$ route with net energy efficiency of 52.3%. No matter for methanol or liquid ammonia, the production process using natural gas as raw material has the highest energy efficiency, while the production process using coal as raw material has the lowest energy efficiency. In addition, in the case of the same raw material, the energy efficiency of methanol preparation process is higher than that of ammonia preparation process. It can be explained by the fact that the Haber-Bosch process in ammonia production requires a large amount of electricity and steam, leading to lower energy efficiency. Table 1 shows that the energy utilization efficiency of PV/CCU-$CH_3OH$ route (50.3%) and PV-$NH_3$ (43.9%) is not high, indicating that the application of renewable energy technology and carbon dioxide capture technology cannot significantly improve the energy utilization performance of methanol or ammonia preparation process. In the scenarios of producing fuel from renewable $H_2$, energy consumption is concentrated in the $H_2$ generation process, mainly because water electrolysis requires a considerable amount of electricity. By coupling the renewable energy power generation process with $H_2$ generation process, the problem of high energy requirement can be greatly alleviated, and it can also help to absorb excess renewable energy production capacity.

## 3.2 | LCA results and impact analysis

Table 2 lists generated GHG emissions of the two fuels during the production stage under different scenarios and the results reported by previous studies. By comparing the calculated results in the present work with those in the literatures, we can find that the present results agree well with the literature data in general, which validates the reliability of the present method.

Figure 4A,B illustrate the GWP balance of full supply chain of fuels per kg and MJ, including production, transportation, and utilization stage of methanol and ammonia. For ammonia, GHG emissions are mainly concentrated in the fuel production phase, while transportation and utilization phases contribute little to the greenhouse effect. Methanol, on the other hand, emits a considerable amount of $CO_2$ when burned in the internal combustion engine, resulting in a large GWP in the utilization phase. As shown in Figure 5A, in NG-$CH_3OH$ and PV/CCU-$CH_3OH$, GHG emissions in fuel utilization stage account for 61.71% and 56.55% of total GHG emissions through the whole life cycle, respectively. Although methanol is considered as a clean fuel compare with conventional fossil fuels such as gasoline and diesel, it still contains a certain amount of carbon, which will be converted into $CO_2$ during combustion process and released into the atmosphere. On the other hand, ammonia is a carbon-free energy carrier with almost no direct

**TABLE 2** Literature comparison of GHG emissions of energy carriers in their production phases

| Production phase | GHG emissions (This study) | Reference |
|---|---|---|
| Coal-$CH_3OH$ (kg $CO_2$-eq/kg) | 3.09 | 2.6 to 3.8[39] |
| NG-$CH_3OH$ (kg $CO_2$-eq/kg) | 0.84 | 0.873 to 0.881[40] |
| PV/CCU-$CH_3OH$ (kg $CO_2$-eq/kg) | 1.04 | 0.99[41] |
| Coal-$NH_3$ (kg $CO_2$-eq/kg) | 3.93 | 3.85[22] |
| NG-$NH_3$ (kg $CO_2$-eq/kg) | 2.70 | 2.74[13] |
| PV-$NH_3$ (kg $CO_2$-eq/kg) | 0.78 | 0.93[42] |

**TABLE 1** The energy analysis for the six scenarios

| | Coal-$CH_3OH$ | NG-$CH_3OH$ | PV/CCU-$CH_3OH$ | Coal-$NH_3$ | NG-$NH_3$ | PV-$NH_3$ |
|---|---|---|---|---|---|---|
| Energy consumption | MJ | MJ | MJ | MJ | MJ | MJ |
| Heating value of feedstock | 33 989.05 | 22 989.9 | \ | 29 215.98 | 22 037.9 | \ |
| Raw material acquisition | 256.24 | 2802.1 | 39 485.38 | 220.1 | 2686.4 | 35 438.1 |
| Methanol/Ammonia production | 8304.1 | 7196 | 154 | 13 300 | 11 060 | 7200 |
| Total | 42 549.39 | 32 988 | 39 639.38 | 42 736.08 | 35 784.3 | 42 638.1 |
| Energy efficiency | 46.8% | 60.4% | 50.3% | 43.8% | 52.3% | 43.9% |

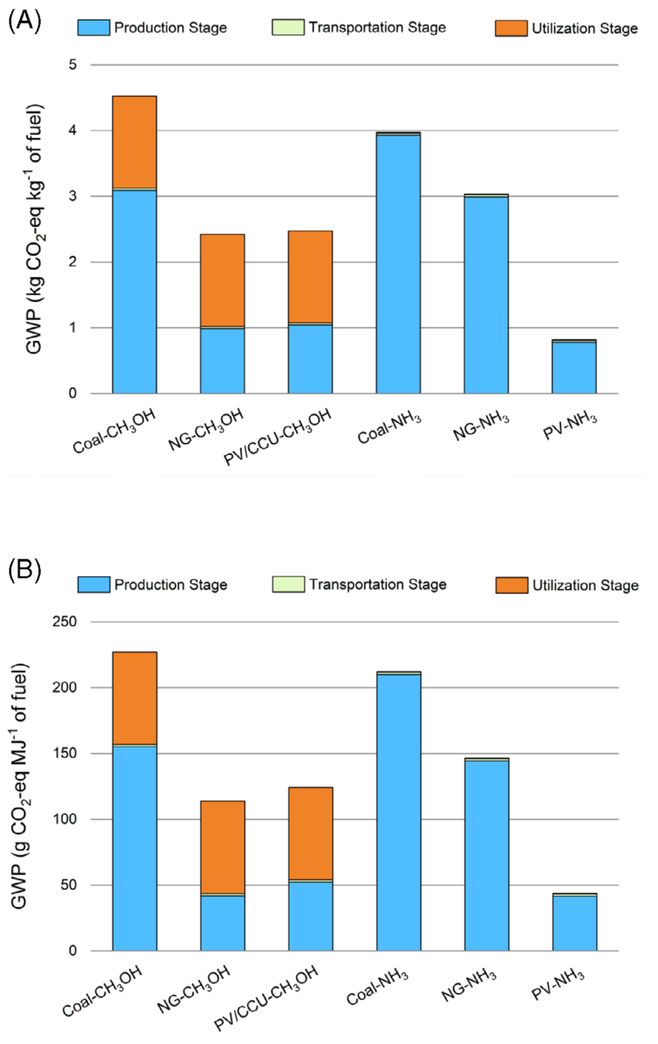



**FIGURE 4** Total GHG emissions from the entire supply chain of energy carrier under various scenarios, A, per unit mass and B, per unit energy

greenhouse gas effect. This is the main reason for the above differences.

Considering complete life cycle, Coal-$CH_3OH$ and Coal-$NH_3$, which use coal as raw material to manufacture $H_2$ carriers, have the highest GHG emissions. When 1 kg or 1 MJ of methanol is produced from hard coal and transported 1500 km away by rail and finally used in the internal combustion engine, it emits around 4.52 kg or 227.05 g of CO2-eq, respectively. For 1 kg or 1 MJ of ammonia, this quantity of emissions slightly reduces to 3.97 kg or 212.36 g of CO2-eq, respectively. Using natural gas to produce $H_2$ carriers has a significant effect on reducing GHG emissions, especially for methanol. In NG-$CH_3OH$, producing 1 kg methanol emits about 0.84 kg $CO_2$-eq, which is approximately 73% less than in Coal-$CH_3OH$.

Manufacturing methanol using captured $CO_2$ and renewable $H_2$ as feedstock offers an effective solution to reduce fossil energy resource consumption. Hydrogenation of $CO_2$ to methanol via CCU technique can save GHG emissions by 66% compared to Coal-$CH_3OH$, but this quantity of emissions increases by 24% compared to NG-$CH_3OH$. Although CCU technique can capture $CO_2$ and use it as raw material for value-added products, it cannot be considered as an effective solution for long-term storage of $CO_2$. When these $CO_2$-based products are used after a short period, for example burned in the internal combustion engine, they will emit back its incorporated $CO_2$ into the atmosphere.[43] In addition, capturing $CO_2$ requires extra electricity and steam, which indirectly lead to increase GHG emissions. Consequently, in terms of reducing GHG emissions, the production of methanol based on CCU technique has no obvious advantages compared with the conventional methanol production from natural gas. However, $CO_2$ capture unit can absorb $CO_2$ in the exhaust gas of the boiler, thereby reducing the GHG emissions of the power plant that provides electricity and steam for methanol synthesis. If the proportion of the flue gas treated by $CO_2$ capture plant in the total flue gas of the carbon capture power-plant (close to zero in present work) continue to increase, the life cycle GHG emissions of the methanol production route based on CCU technique will correspondingly reduce. This content will be further discussed later in Section 3.4.

In all the investigated scenarios, the route of ammonia production via electrolysis of PV solar has lowest GHG emissions, which are 80% and 71% less than coal-to-ammonia route and natural gas-to-ammonia during the production phase, respectively. Regardless of whether it is calculated by unit mass (kg) or unit energy (MJ), electrolysis-based ammonia production has the lowest GWP throughout the full supply chain, at 0.82 kg of $CO_2$-eq/kg of ammonia and 43.87 g of $CO_2$-Equation $MJ^{-1}$ of ammonia.

As the production phase has a significant contribution to the GHG emissions of the whole supply chain, and compared with the transportation phase and utilization phase, the systems and processes in the production phase are more complex, so it is necessary to analyze the carbon footprint of each subsystem of the production phase in each scenario. As shown in Figure 5, the left pie chart represents the emission distribution of the $H_2$ carrier supply chain and the right one shows the distribution of the GHG emission in production phase. In the scenarios where coal is used as feedstock to manufacture $H_2$ carrier, syngas production contributes the most to the greenhouse effect, which is consistent with the conclusion of Qin et al.[44] Taking coal-to-methanol as an example, the GHG emissions during syngas production account for 74.53% of the total emissions. In the gasifier, carbon in the coal is converted into CO, $CO_2$, $CH_4$, and

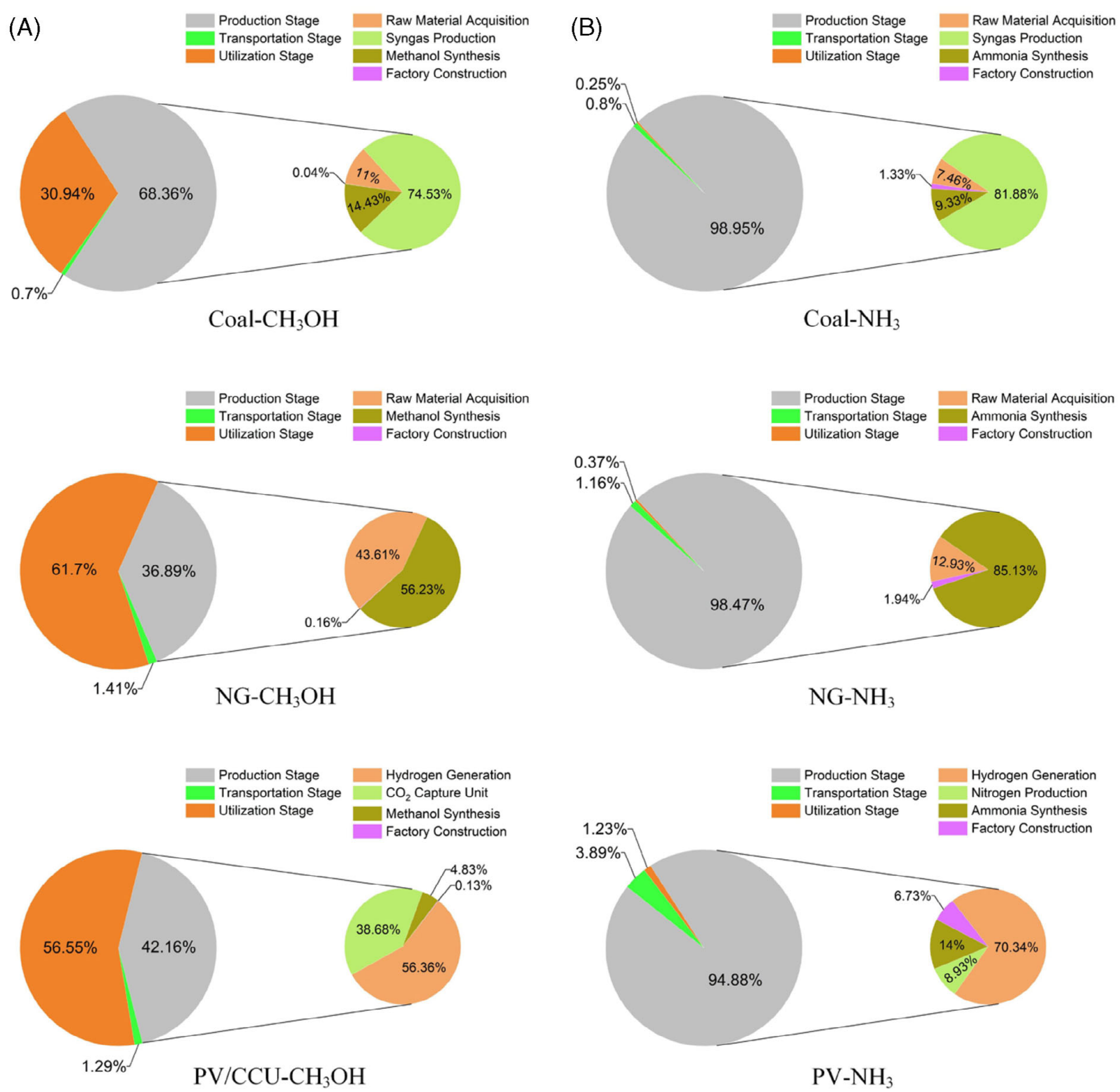



**FIGURE 5** GHG emissions distribution of A, methanol and B, ammonia supply chain under various scenarios

other species through a serial of complex reactions. Due to the characteristics of coal rich in carbon and less in hydrogen, the $H_2/CO$ molar ratio of crude syngas from coal varies between 0.2 and 1.0, far less than target of 2.05 to 2.15,[45] so the hydrogen content in the crude syngas need to be improved via water-gas shift (WGS) reaction. In the WGS unit, CO and stream can be reacted in the presence of catalyst to form $H_2$ and $CO_2$, the reaction equation is as follow:

$$CO + H_2O \rightarrow H_2 + CO_2 + Q, \quad (2)$$

However, WGS unit converts CO to $CO_2$, most of which is not used as feedstock for methanol synthesis but is separated from syngas by Rectisol wash process[46] and finally discharged into the environment. The diagram of Rectisol wash process is shown in Figure 6.

Compared with coal-to-methanol, the share of GHG emissions coming from syngas production and methanol synthesis processes decreases significantly from 88.96% to 56.23%. Due to the intrinsic properties of feed natural gas, the $H_2/CO$ molar ratio of crude syngas produced by steam reforming is higher than that of syngas produced by coal gasification, which means that the greenhouse gas generated from WGS unit reduces and ultimately the amount of greenhouse gas released from Rectisol wash unit is accordingly reduced.

In PV/CCU-$CH_3OH$ and PV-$NH_3$, hydrogen generation replaces syngas production as the process with the largest contribution to the greenhouse effect during fuels

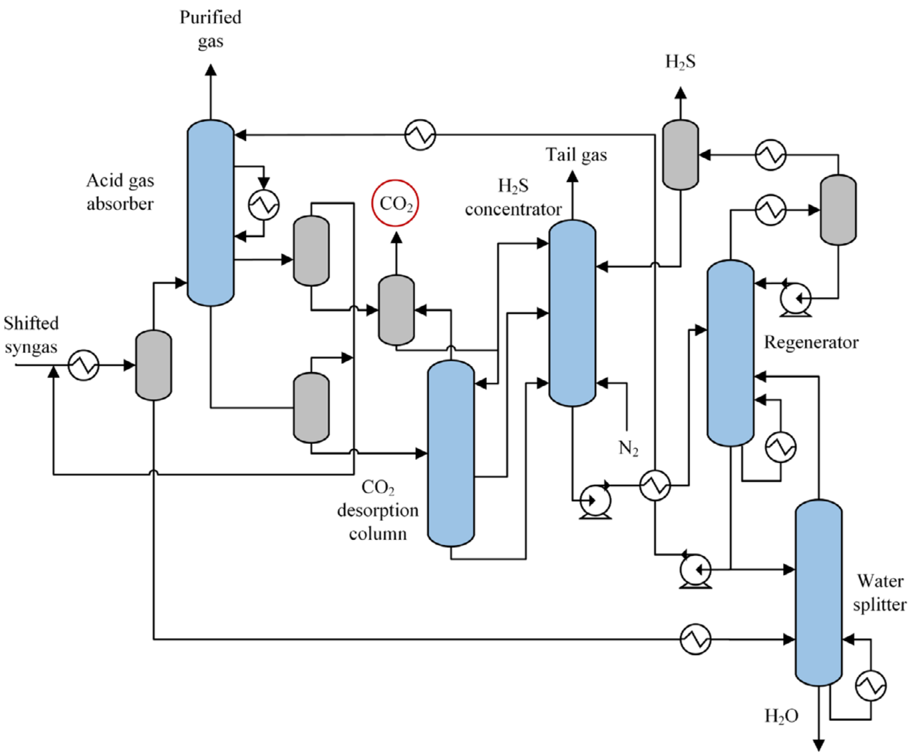



**FIGURE 6** Rectisol process for $CO_2$ and H2S removal

production phase. Water electrolysis is an energy-intensive process that consumes a large amount of electric power.[47] Even when renewable is used as the source of electricity, the process of generating hydrogen through water electrolysis is still the largest contributor to greenhouse effect during the fuel production phase. When hydrogen is obtained through water electrolysis, the process of syngas production can be displaced. Besides, a renewable source of electricity can play a significant role in mitigating GHG emissions. Therefore, combining these two reasons, the greenhouse effect of PV-$NH_3$ is the lowest among all scenarios.

## 3.3 | Sensitivity analysis

To investigate more deeply the impact of each input parameter on global warming potential under different scenarios, sensitivity analysis (SA) is performed using a one-at-a-time approach (OAT). In this study, each input parameter is changed by $\pm10\%$ to evaluate the sensitive effect. Figure 7 represents the sensitivity results of input parameter at production phase in different scenarios. In the case of fuel produced by conventional methods, taking coal gasification for example, the result clearly shows that coal consumption is the dominant factor to the greenhouse effect in the production phase. This is mainly because direct emission is the largest contributor to GHG emissions and it basically comes from the carbon in the feed coal. In addition, steam is also an essential parameter that has a considerable impact on GHG emissions. Similar to the situation in Coal-$CH_3OH$ and Coal-$NH_3$, natural gas and steam are the two most sensitive parameters in the route of fuels produced from natural gas. The main difference is that the sensitive degree of steam increases markedly, meaning that steam supply has a greater impact on GHG emissions at the fuel production stage. In the scenarios of using renewable $H_2$ to produce fuel, $H_2$ consumed in the fuel synthesis process is the most sensitive input parameter, whose sensitivity degree are attained to $\pm5.6\%$ and $\pm7.0\%$ in the scenario A-3 and scenario B-3, respectively. As mentioned above, the supply of electricity plays a vital role in $H_2$ production. From the perspective of sensitive analysis, the sensitivity degree of electricity consumed in the $H_2$ production is roughly equal to that of hydrogen used in the methanol synthesis, which again confirmed that point of view. $CO_2$ is another essential input parameter in the PV/CCU-$CH_3OH$ route. The influence of steam consumed in the $CO_2$ capture unit on GHG emissions also cannot be ignored.

## 3.4 | Improvements

As China is rich in coal but poor in natural gas and oil, coal occupies a dominant position in energy structure.[5] Therefore, adopting coal as raw material to manufacture commercial chemicals is the main technique route now

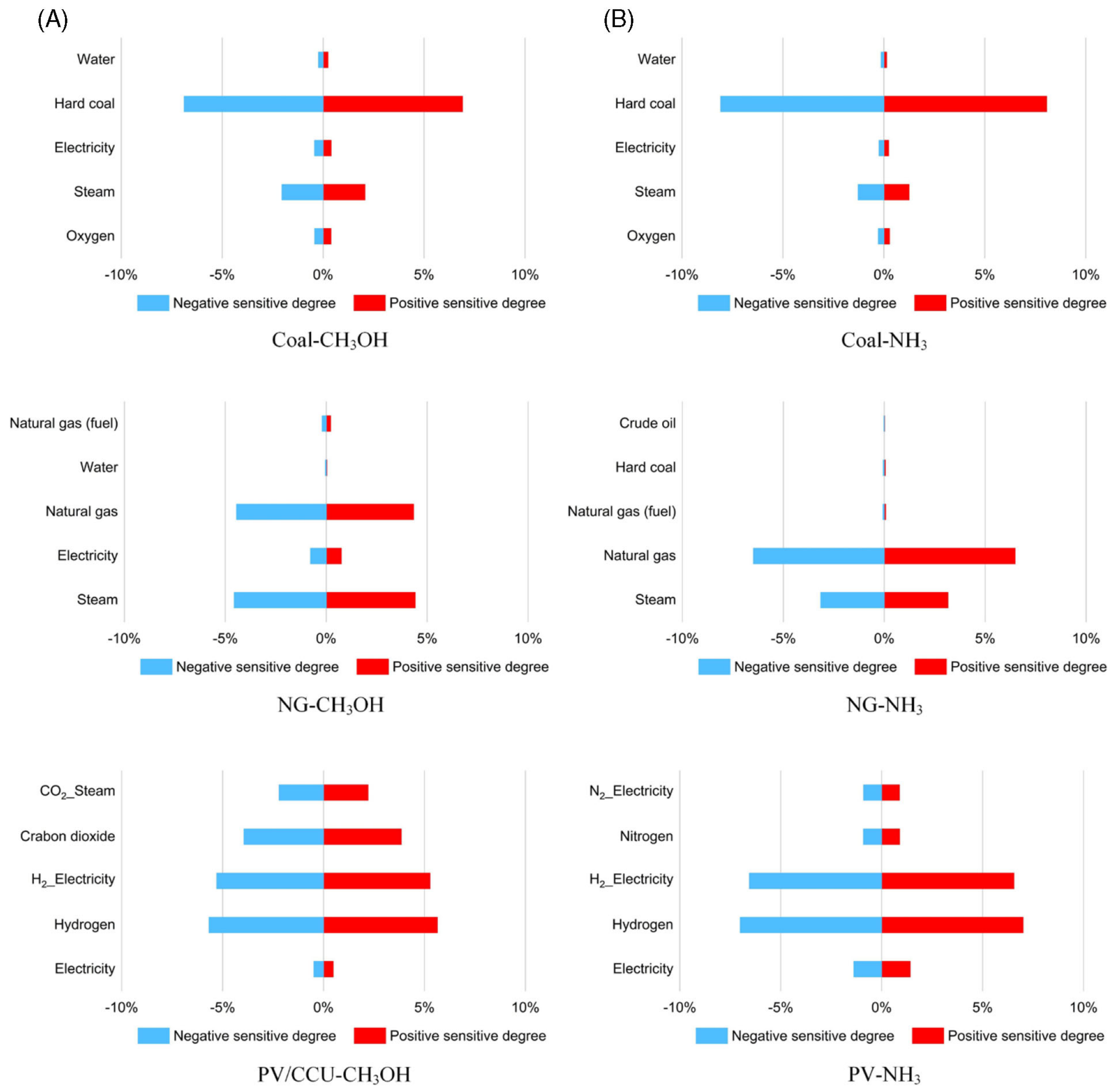



**FIGURE 7** Sensitivity results of various fuel production routes input parameter

in China. However, the life cycle emissions of coal-based methanol and coal-based ammonia are more serious compared to other routes, mainly due to the direct emission during syngas production process. Carbon capture and storage (CCS) represents a key solution to reduce GHG emissions by separating $CO_2$ from industrial or related source and transporting it to storage sites, where it is isolated from the environment for a long period of time.[48] In present study, there are two main sources of GHG emissions in the fuel production stage, one is the tail gas from Rectisol in the acid gas removal (AGR) unit, the other is the flue gas emitted from power plant. The concentrate of $CO_2$ in the former can reach more than 97%, so that it can be directly compressed for storage after moisture separation, while the $CO_2$ in the latter need to be captured before compression because of its low component concentration. The key parameters for the $CO_2$ compression and storage are presented in Table S3, which is collected from prior literature.[49]

Figure 8 represents a comparison of the life cycle emissions of coal-to-methanol (CTM) and coal-to-ammonia (CTA) with/without CCS in the production stage. The emission penalty in the figure represents the additional emissions resulting from the incorporation of CCS system into the methanol/ammonia plant. When methanol/ammonia plant is retrofitted with CCS, GHG emissions from the original methanol/ammonia production chains are decreased by 81.02% and 85.87%, while additional 19.12% and 18.97% of emissions need to be paid for maintaining the operation of $CO_2$ capture and

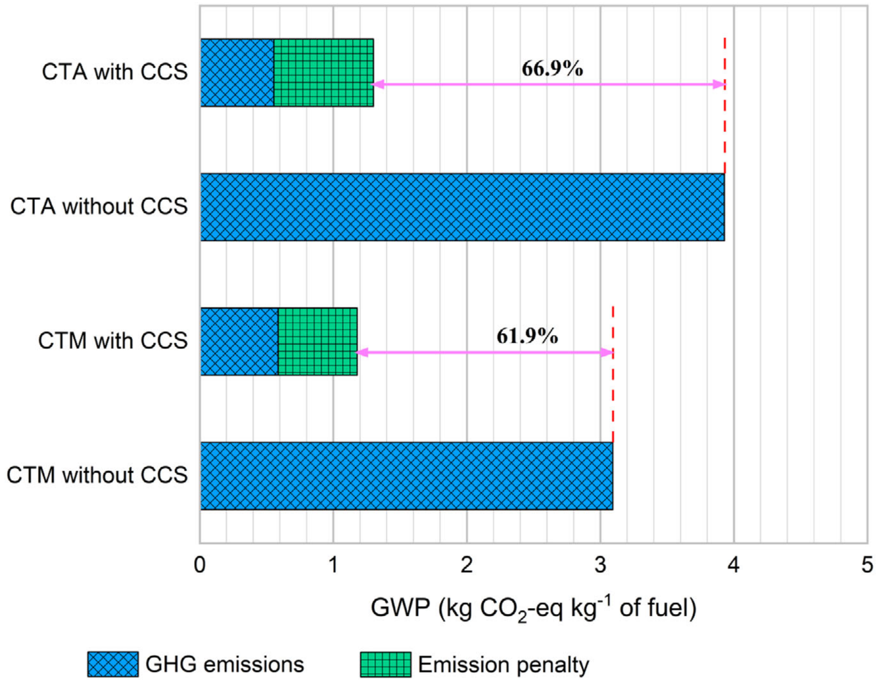



**FIGURE 8** Life cycle assessment results for CTM and CTA with/without CCS

**TABLE 3** Life cycle assessment results of PV/CCU-$CH_3OH$ route with increasing flue gas capture rate

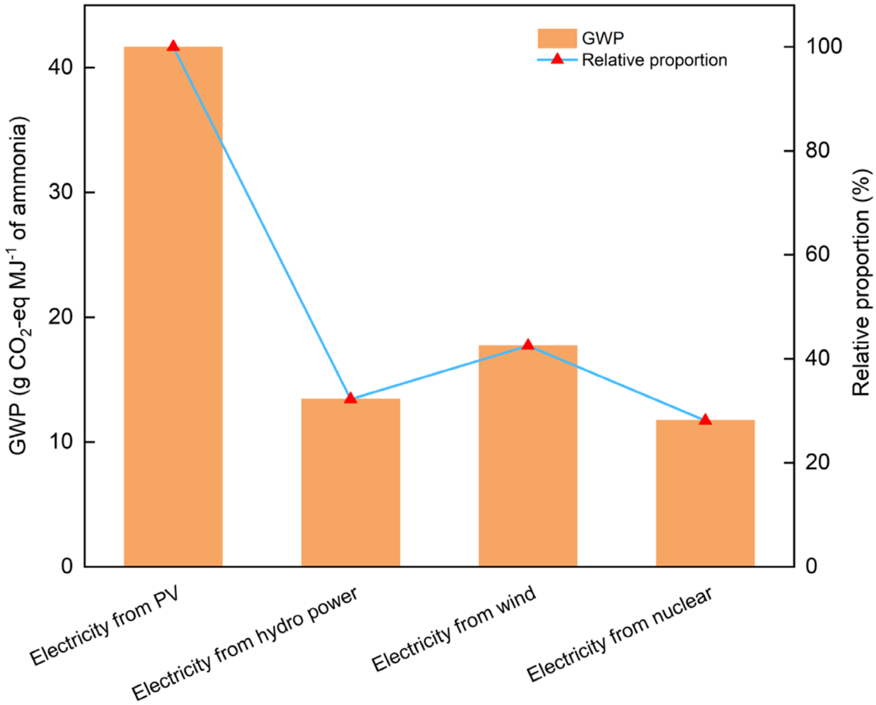
| GHG emission | 0% (Approximate) (g $CO_2$-eq/kg fuel) | 50% (g $CO_2$-eq/kg fuel) | 100% (g $CO_2$-eq/kg fuel) |
|---|---|---|---|
| Carbon dioxide capture unit | 403.72 | 244 | 84.6 |
| Methanol synthesis | 51.72 | 31.8 | 12 |
| Total emission | 1043.65 | 864 | 685 |

storage, that is, the net carbon reduction efficiency of methanol/ammonia plant with CCS are 61.9% and 66.9%, respectively. In general, CCS is an important way to efficiently reduce the GHG emissions in conventional methanol/ammonia production route.

Capturing $CO_2$ and transforming it into valuable chemicals using renewable $H_2$ is becoming a promising solution to mitigate global warming and ensure energy security.[50] However, the PV/CCU-$CH_3OH$ has higher GHG emissions compared to NG-$CH_3OH$ route. According to the sensitive analysis, $CO_2$ capture process plays a significant role in the greenhouse effect mainly due to high steam consumption. In this work, since the flue gas treated by CCS system only accounts for less than 5% of total flue gas emitted from power plant, it is approximately considered that the emission inventory of coal-fired power plant matched with CCS system is consistent with that of power plant without CCS. If the capture capacity of CCS system can be further expanded, the amount of $CO_2$ in the exhaust gas emitted from power plant will be reduced. Thus, for PV/CCU-$CH_3OH$ route, there is still some room for further optimization of its environmental performance. Table 3 lists the GHG emission during methanol production in scenario A-3 when the flue gas capture rate (the proportion of captured fuel gas to the total flue gas) is 0%, 50%, and 100%, respectively. When all the exhaust gas from power plant is treated by $CO_2$ capture unit, GHG emissions reduce by 319.12 g of $CO_2$-eq/kg of methanol in $CO_2$ capture process. Considering the global warming potential of the entire methanol production phase, 34.4% of GHG emissions are reduced compared to the result of scenario A-3 in the Section 3.2. Conclusively, if existing power plant carbon capture system can be scaled up so that all flue gas passes through the capture unit, the GHG emissions level of CCU-based methanol production route is comparable to that of solar PV-based ammonia production route.

all the scenarios, there may be still some space for further improvement. The construction process of photovoltaic plant is the main factor causing energy consumption and GHG emissions, so the environmental performance of PV-$NH_3$ scenario can be improved by optimizing relevant processes in construction process of photovoltaic power station or choosing other clean electricity generation source for water electrolysis. Figure 9 shows the

FIGURE 9 Carbon footprint evaluation results after power optimization




mitigation potential of greenhouse effect in the solar PV-based ammonia production route with the improvement of electricity generation. If solar photovoltaic power generation is replaced by other renewable sources of power, the mitigation potential is obvious. For example, there is a 57.5% reduction in GHG emission when wind power is used to generate electricity. Similar results can be obtained if hydro power or nuclear is applied.

## 4 | CONCLUSIONS

Green $H_2$ carrier liquid fuel is a potential solution to both energy crisis and environmental pollution in the future. Investigating carbon footprint of these liquid fuels over their complete life cycle can provide an intuitional environmental assessment. In present work, we conduct an LCA study on the full supply chain of two promising $H_2$ carrier liquid fuels that is, methanol and ammonia, covering production, transportation, and utilization phases. An energy analysis review concludes that natural gas-to-methanol route has the highest energy efficiency. Fuels production using renewable $H_2$ have not performed well in terms of energy efficiency, mainly due to the large power consumption of water electrolysis. The results of life cycle emissions show that production phase is the largest contributor to GHG emissions in most scenarios. For methanol, the utilization phase has an important contribution to overall emissions, while the utilization phase contributes little to overall emissions in the ammonia supply chain. Considering the completed life cycle, solar PV-based ammonia production route emits 43.9 g of $CO_2$-Equation $MJ^{-1}$ of ammonia, which has the lowest greenhouse effect in all scenarios. In the case of fuel production using conventional manufacturing method, syngas production process generates the most greenhouse gas, followed by fuel synthesis process. However, in the scenarios of using renewable $H_2$ to produce fuel, $H_2$ generation process replaces syngas production process to become the most GHG emissions during fuel production phase.

Furthermore, a sensitivity analysis was performed to figure out the key factors which influence the impact evaluation results in fuel production stage. Sensitivity analysis indicates that coal consumption is the key parameter to the global warming potential in the coal-based fuel production route due to direct emissions during syngas production process, while electricity is the key contributor to influence GHG emissions in renewable $H_2$-based fuel production route, especially the electricity consumed in $H_2$ generation process. Based on the results of sensitivity analysis, we propose some measurements to improve environmental performance. The CCS technologies can dramatically reduce the life cycle GHG emissions though it causes the extra energy demand for $CO_2$ capture, transportation, and storage. With the electricity optimization, the life cycle emissions in the solar PV-based ammonia production route have been significantly reduced. We find that GHG emissions can be reduced by 57.5% with electricity from wind power.

With the implementation of a new round of energy industry planning, China is accelerating the transition process of clean energy, and the demand for decarbonization and emission reduction is increasing day by day. As mentioned above, ammonia has been centered great expectations as a net zero emission society enabler. At present, the dominant use of ammonia is still in the fertilizer industry, and its application for power needs to be further explored. Governments agencies and industry investors should consider appropriate capital investment to support follow-up high-quality research.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## DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.


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