Hydrogen production via ammonia from methane integrated with enhanced oil recovery: A techno-economic analysis

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Abstract: The paper aims to evaluate the hydrogen production from methane, transported as ammonia, and integrated with CO_2 utilisation in terms of energy, carbon emission and economic analysis. The common alternative for CO_2 utilisation i.e. enhanced oil recovery is adopted for the assessment, which extracts crude oil using captured CO_2. Mass and energy balance of ammonia production are simulated in Aspen plus. Oil extracted by enhanced oil recovery and CO_2 emitted are evaluated based on simplified model using information provided in the literature. Results show that total CO_2 emission in hydrogen production with carbon capture and enhanced oil recovery could be reduced by 54.8% when compared with conventional oil production, which is from 97.4 tonne·h^{-1} to 44 tonne·h^{-1}. In addition, the cost of hydrogen is significantly reduced by using liquid ammonia as a carrier for transportation. Considering the revenue by selling CO_2 from 0 to 50 \$·tonne^{-1}, the cost of H_2 could be reduced by 9.52% and 14.63% when gas prices are 10 \$·MMBTU^{-1} and 2 \$·MMBTU^{-1}, respectively. It is demonstrated that the revenue for selling CO_2 is an opportunity to reduce carbon emission which could accelerate hydrogen technology incorporated with carbon capture and utilisation in the industry.

Keywords: Hydrogen, Ammonia transportation, CO_2 utilisation, Enhanced oil recovery

Nomenclature

CC	Carbon capture
CCS	Carbon capture and storage
CCUS	CO_2 capture, utilisation and storage
CEPCI	Chemical engineering plant cost index

CHP	Combined heat and power
CU	CO_2 utilisation
EOR	Enhanced oil recovery
FCI	Fixed capital cost
GHG	Greenhouse gas
H_2	Hydrogen
HP	High pressure
HRSG	Heat recovery steam generator
i	Interest rate
LP	Low pressure
M	Molar mass ($mol\cdot kg^{-1}$)
m	Mass (kg)
MEA	Monoethanolamine
NG	Natural gas
NH_3	Ammonia
NRTL	Non-random two-liquid model
NO_x	Nitrogen oxides
O&M	Operating and management
SMR	Steam methane reforming
SSP	Solid state polymerisation
s	Entropy ($kJ\cdot kg^{-1}\cdot K^{-1}$)
T	Temperature (°C)
WSR	Water shift reactor
Y	Yield (%)

Superscripts

n	Year

1. Introduction

Global CO_2 emission has been significantly rising with vast potential to cause catastrophic climate change. In the recent Paris Agreement on climate change, a new goal was set to limit temperature rise to 2 °C [1]. In 2017, CO_2 emission by power plants, industries, vehicles and buildings increased by 1.4%, which reached around 32.5 gigatonnes [2]. Besides, industries and governments have paid burgeoning attention to the use of H_2 for internal combustion engines because of the potential to reduce CO_2 emission. There are several ways to produce H_2, e.g. steam methane reforming (SMR) from natural gas, gasification or pyrolysis from coal, and electrolysis by using renewable electricity [3-5]. Although the electrolysis using renewable energy is regarded as a clean technology with nearly zero emission, it also represents the highest H_2 cost [6]. The cost of per kilogram H_2 varies by using different technologies, which is from 0.27 $\$\cdot kg^{-1}$ using the gasification technology, 1.84 $\$\cdot kg^{-1}$ using SMR, to 23 $\$\cdot kg^{-1}$ using photovoltaic electrolysis [7]. The most common solution to produce H_2 worldwide is to use SMR, which accounts for 48% as shown in Fig. 1 [8].

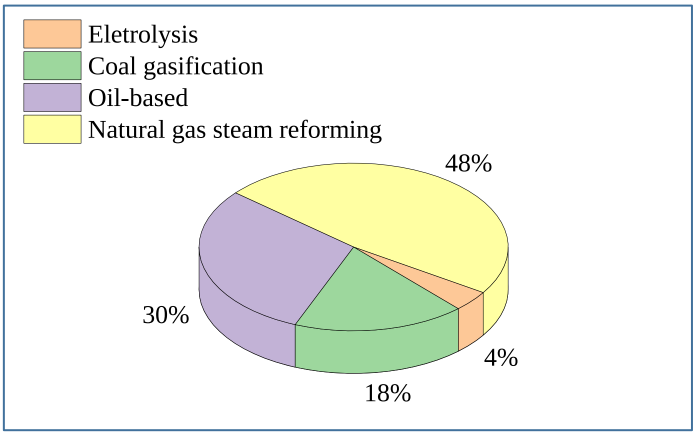

Fig. 1. Percentage of participation methods to produce hydrogen around the world [8].

Compared with the production cost of H_2, a main challenge of its utilisation is its high transportation cost, which is almost twice higher than its production cost via SMR [9]. The cost of transportation represents 60% of the total cost of H_2 [10]. The way to transport hydrogen could be classified according to its physical state i.e. gas, liquid and solid. Currently, gas H_2 transportation by using the pipeline and liquid H_2 transportation by using tank truck are two common methods. Pipeline H_2 transportation is usually realised by embedding a seamless steel pipe system in the underground. The pressure of H_2 in the pipeline is about 40 bar, and the conveying speed could reach 20 $m\cdot s^{-1}$. Pipeline H_2 transportation has the advantages of high speed and high efficiency, but the initial investment is relatively high, and more policy restrictions are concerned during the construction process. Comparably, liquid hydrogen transportation is to convert hydrogen into a liquid at a low temperature of -253 °C and deliver it by tank truck [11]. Compared with high-pressure gaseous transportation, liquid hydrogen has a higher volumetric energy density, and thus transportation efficiency could be greatly improved. For example, the water tanker that is commonly used abroad can reach a water volume of 65 m^3, and can be loaded with liquid hydrogen of about 4,300 kg in a single load. The transport capacity is 10 times higher than that of a bundled tube bundle trailer. However, the hydrogen liquefaction energy consumption is relatively high, which is equivalent to about 33% of the calorific value of the liquefied hydrogen [12]. Meanwhile, it has extremely high heat preservation requirements during transportation to prevent liquid hydrogen from boiling. Comparably, liquid ammonia acts as a carrier for transportation is desirable and cost-effective since it is a well-established technology, which could be considered as the first step of H_2 production via SMR [13].

As a product from methane, ammonia integrated with CO_2 capture, utilisation, and storage (CCUS) is expected to be an alternative way that could reduce the CO_2 emission to nearly zero i.e. similar level as electrolysis technology [14, 15]. During the ammonia production, high purity of CO_2 is generated as an intermedium process. Additional CO_2 is generated for burning additional fossil fuel to increase the temperature in the SMR reactor as well as to generate steam and electricity used for the process [16]. Unlike power plants, the industrial sectors such as hydrogen and ammonia have not experienced high interest on carbon capture and storage (CCS) due to its high associated costs and no economic incentive [17]. There are opportunities for CO_2 utilisation (CU) on ammonia production because CO_2 concentration in the flue gas is higher than those in other processes e.g. power plants and cement. CO_2 from ammonia plant at high purity is ready for CU e.g. enhanced oil recovery (EOR), polymers, urea, CH_4, and methanol [18, 19]. CU could reduce the cost of capturing additional CO_2 and its storage even when CU faces the challenges e.g. low energetic level and reactivity [20]. Typically, this low reactivity can be overcome by high-energy reaction partners. When evaluating the overall energy balance and efficiency of the process, the energy used to generate these materials has to be taken into account because it is related with the CO_2 emission. Nowadays, there are some current and planned EOR projects as indicated by the reference [21], most of them are located in US, Canada, China, Norway, Abu Dhabi and United Arab Emirates.

Considering the status of hydrogen production, transportation and the concerning CCUS, this paper aims to investigate the integrated process i.e. H_2 production is from methane with ammonia as a carrier for H_2 transportation and combined with EOR, which is shown in Fig. 2. CO_2 emission generated in the proposed process is analysed to reduce the cost of H_2 by considering the revenue for selling CO_2. It contributes the first comprehensive evaluation in aspect of energy, environment and economy though several research studies have demonstrated the technical and economic advantages of each separated process. The framework of this study is organised as follows: each step of the integrated process i.e. ammonia production via SMR, EOR and the ammonia transportation is respectively illustrated. After that, economic analysis is carried out, which includes a sensitivity analysis in terms of a range of CO_2 selling price for utilisation and natural gas price. Since ammonia production from methane reformer is sensitive to natural gas prices, the conclusions are robust over a range of fuel prices and CO_2 prices.

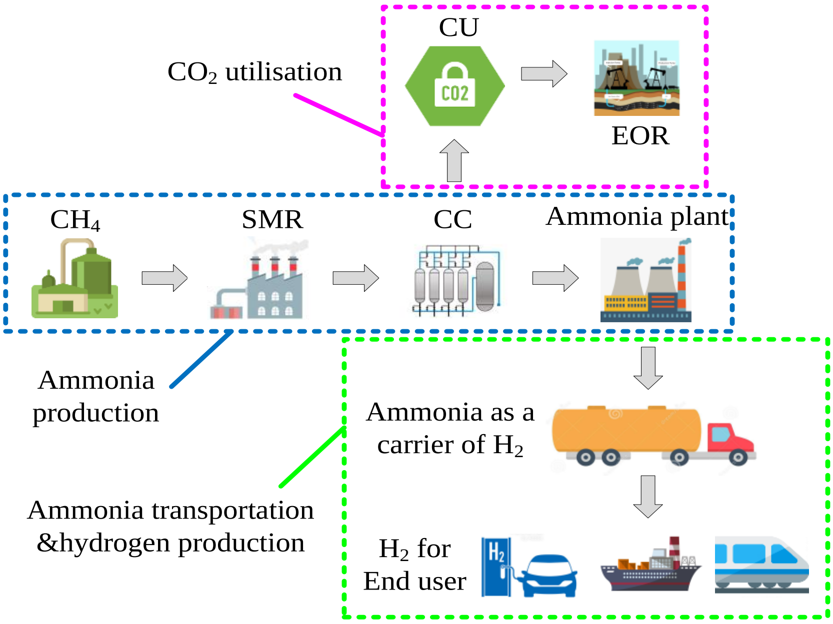

Fig. 2. Hydrogen production using ammonia as its carrier for transportation and EOR.

2. Methodology

A detailed assessment of the proposed integrated process is carried out in terms of three sections: H_2 production, ammonia plant via the Haber-Bosch process, and CCUS via EOR. H_2 cost is evaluated regarding the cost of ammonia production, transportation, and the revenue for selling CO_2. The production process is simulated in Aspen plus to determine the mass and energy balance which is based on an ammonia plant with the capacity of 1270 $tonne \cdot day^{-1}$. The amount of the CO_2 generated from the ammonia plant is used to quantify the amount of oil production and its CO_2 emitted. In each section, the methodologies and assumptions considered to estimate the mass and energy balances are described before presenting the results.

2.1 Ammonia production

The production of ammonia adopts a well-stablished SMR process, which is generally composed of the SMR reactor, water shift reactor (WSR), as well as CO_2 separation, methanator, compression, and ammonia reactor.

Reactions (1) and (2) occur in the SMR and WSR reactors, respectively [22]. Table 1 presents operating parameters and assumptions used in the simulation of the SMR, WSR, and CC [23].

$$CH_4 + H_2O = CO + 3H_2 \tag{1}$$

$$CO + H_2O = CO_2 + H_2 \tag{2}$$

Table 1. Operating conditions of the SMR process.

Parameters	Steam	NG	SMR	WSR	CC	Assumptions	Values
Efficiency (%)					80[24]	Steam/CH_4	3[8, 24]
Conversion (%)			83	73		Overall efficiency (%)	70
Pressure[25] (bar)	30	28.5	19.5	18	17	CO_2 purity (%)	95.00
Temperature[25] (°C)	510	510	950	419[22, 25]	38		

The schematic diagram of the whole SMR process is shown in Fig. 3 which is simulated by using Peng Robinson's equation [22] and all reactors were defined in Aspen Plus as stoichiometric reactors where the reactions 1-6 are introduced in each of them. The detailed processes are illustrated as follows: first methane (CH_4) is mixed with the steam at 510 °C and 30 bar. The mixed components enter primary SMR reactor where reaction (1) occurs. After that, compressed air is mixed with exhaustive flue gas from primary SMR and flows to the second SMR reactor. O_2 that comes from the air reacts with the remaining CH_4 to increase the temperature to 950 °C, and N_2 is used to produce ammonia. The syngas basically composed of CO, CO_2, H_2, CH_4, and H_2O is cooled down to 350 °C and exchanges heat with feed water used in the SMR. The reaction (2) occurs in the WSR, and the syngas is cooled at 38 °C. Then CO_2 is separated from flue gas in an absorber column by using monoethanolamine (MEA) where the efficiency is around 80% to achieve the purity of 95%. The syngas that contains H_2 is delivered at 17 bar to the methanator [25]. CO_2 and CO are poisons for many types of catalysts. Thus, the residual CO and CO_2 after cleaning the flue gas from CO_2 must be removed from the syngas which are converted to methane and water, as presented in Reactions (3) and (4), through a nickel or ruthenium catalyst with H_2 in the Methanator.

$$CO + 3H_2 = CH_4 + H_2O \tag{3}$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O \tag{4}$$

First, SMR reported by Simbeck [26] is reproduced to validate the model and to estimate the efficiency of SMR and WSR. After that, the model is used and updated to the capacity of 1,270 tonne·day^{-1} of ammonia based on the industrial and commercial size reported by Olateju [7]. Additional assumptions considered in SMR are elaborated as follows: (1) Composition of natural gas is 100% methane; (2) The separation of water in the condenser is complete; (3) Heat losses through the equipment are neglected.

The final step is the ammonia production which consists of the following steps: syngas compression and the ammonia process. The syngas contains high percentage of H_2 and N_2, which is compressed at 202.6 bar [27] and it is delivered to the finally reactor where Reaction (5) takes place.

$$N_2 + 3H_2 = 2NH_3 \tag{5}$$

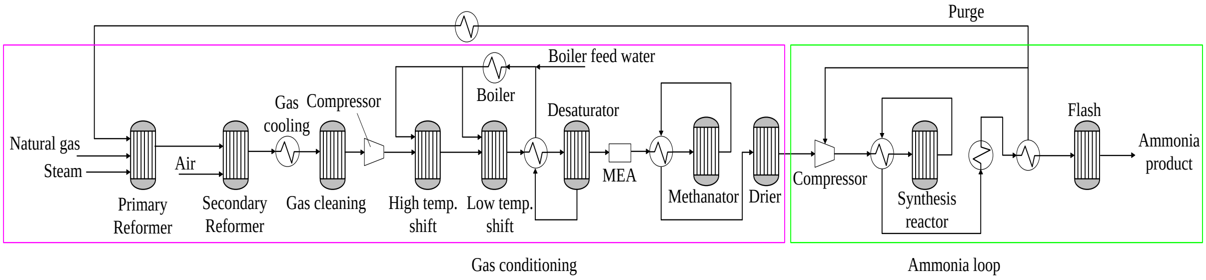

Fig. 3. Schematic diagram for the ammonia production simulation.

CO_2 is removed in a MEA-based capture plant. It consists of an absorber where the CO_2 is captured by the amine solvent and a stripper where the CO_2 is separated from the MEA solution. To determine the optimal design condition of the capture plant, there are some parameters that have to be evaluated and defined such as size of the absorber, lean and rich loading, temperature and pressure in the stripper. Aspen Plus software has been used to simulate the capture plant mainly to assess the thermal heat required in the capture plant. Simulation is based on 30 wt% monoethanol amine (MEA) solvent. The applicability of the Aspen Plus simulation has been validated at full load by various research studies to evaluate this particular solvent [28]. Therefore, only the approach to full load design optimisation is discussed in this part. The methodology to optimise the design of the CO_2 capture plant is illustrated as follows:

1. The lean solvent loading of the MEA solution is varied to realize the minimum energy in the reboiler.
2. While studying the effect of different lean loadings, the stripper reboiler pressure is varied to change the values of the lean loading and the temperature is kept constant at 120 ºC [29].
3. The absorption solvent circulation rate is varied to achieve the targeted CO_2 removal capacity (90%).

Related to the compressor, it consists of a gear-type centrifugal compressor with several stages to compress the CO_2 stream, as suggested by Siemens [30]. The number of stages depends on the pressure ratio which is used to compress CO_2 from 2 bar to 110 bar, i.e. with a pressure ratio of 55, six stages are needed [31]. If pressure ratio is higher than 55, more compressor stages might be necessary. In this paper, CO_2 is compressed from 1.9 bar to 150 bar for the purpose of EOR [32]. The pressure ratio is around 80, and therefore one more stage is needed. The configuration of the CO_2 compressor shown in Fig. 3 is selected with two trains of a gear-type centrifugal compressor with seven stages and intercooling after each stage as it is designed for a nominal pressure ratio of 80 and a CO_2 temperature of 40 °C after the intercoolers based on the information in the references [31, 33].

2.2 Ammonia as a carrier for H_2 transportation and reproduction

It is recognised that ammonia is an important agricultural basic product and chemical raw material which can be transported through traditional low-pressure tank trucks with small and medium scale for transportation. Also, it could be transported by using rail tanker and the existing pipeline network of ammonia supply. In this section, liquid ammonia is considered as a carrier for hydrogen transportation. Although the cost of ammonia transportation is significantly lower than the other routes of hydrogen transportation, ammonia transportation requires additional investment costs for hydrogen reproduction cracker in the hydrogen refuelling station which could refer to Reaction (6).

$$2NH_3 = 3H_2 + N_2 \tag{6}$$

The size of the hydrogen refuelling station is determined by the demand for hydrogen, and the supply capacity of the station is assumed as 500 kg·day^{-1} for further analysis. The total amount matches the results of reforming, change, absorption and purity. Liquid ammonia is supplied to the hydrogen refuelling station by means of low-pressure tank truck transportation. The main assumptions of the transportation phase are shown in Table 2. It is indicated that the common transportation distance by using the liquid ammonia is round 70 km. The main investment cost of the transportation is shown in Table 3 which is composed of the truck, unloading device and trailer. Depreciation period of these device is assumed as 20 years. Then the cost of hydrogen transportation using liquid ammonia as a carrier is evaluated which includes labour cost, fuel cost, operation and management (O&M) cost as well as fixed equipment cost. Fix equipment cost is calcualted by daily investment cost based on hydrogen supply capacaity i.e. 500 kg·day^{-1}. Then the specific transportation costs are shown in Table 4 [34, 35]. Compared with the cost by using gas hydrogen transporation using tank truck [34], the total cost of hydrogen transportation by using liquid ammonia as a carrier could be reduced by 50%, which demonstrates its potential as an ideal solution to transportation in terms of short and medium scales.

Table 2. Main assumptions in liquid ammonia transportation.

Items	Values
Average transportation distance (km)	70[1]
Truck capacity ammonia (kg)	1200[1]
Utilisation percentage (%)	90[1]
Operating pressure (bar)	8[1]
Fuel economy (L· (100 km)$^{-1}$)	20[1]

Analysis cycle (Year)	20[1]
Price of diesel ($\$\cdot L^{-1}$)	0.95[2]

[1] The values come from the standard of China liquid ammonia truck.

[2] The value used is the current price in China considering the current exchange rate.

Table 3. Main investment cost of the transportation [34].

Items	Values ($)	Depreciation period (year)
Truck[1]	5500	20
Unloading device[1]	70000	20
Two trailers[1]	24000	20
Ammonia cracker	4000	20
Total	103500	20

[1] Trailers are considered because the depreciation period of each one is 10 year.

Table 4. O&M cost and fixed cost of liquid ammonia transportation.

Items	Values
labour cost ($\$\cdot kg^{-1}$)	0.05[1]
Fuel cost ($\$\cdot kg^{-1}$)	0.05[1]
Other O&M cost ($\$\cdot kg^{-1}$)	0.18[2]
Total	0.28
Fixed equipment assets ($\$\cdot kg^{-1}$)	0.2[2]

[1] The value is reported by Liu et al. [35]. [2] The value is reported by An et al. [34].

2.3 CO_2 utilisation

EOR is selected as an alternative for CU in this work. The production of EOR is based on the CO_2 produced in the ammonia plant with a capacity of 1,270 tonne·day^{-1}. A general schematic diagram of EOR is shown in Fig. 4. It is one of the potential alternatives for CU and is a technique used to increase the crude oil production extracted from an oil field. The CO_2–EOR has been identified to be profitable in a commercial scale, which could be quite beneficial to the economy in UK [36], United State [37], and Mexico [38]. When the pressure of an oil reservoir is depleted through primary and secondary production, the use of the CO_2 can be a tertiary recovery method. It consists of injecting CO_2 into the reservoir to dissolve in the oil. CO_2 makes the oil reduce the viscosity of the hydrocarbon [39] because the CO_2 is miscible with oil [40]. The amount of oil produced by EOR as well as CO_2 emitted and sequestered from the recovered oil are estimated using basic calculation and information provided in Table 5 which are based on the references [41-43]. Although there are other sources of CO_2 for EOR, a simplified calculation can provide inspiration that is related to CO_2 emission reduction and the benefit for co-production. In this work, the CO_2 accounted is the one generated by burning the oil. It is extracted only by injecting CO_2, which is 0.43 tonne per barrel of oil, and the CO_2 that comes from the ammonia plant does not remain for storage [43]. From the total amount of CO_2 injected, only 60-70% is stored [41], and the rest leaves with the extracted oil. This information is based on a life cycle assessment which includes the whole CO_2 generated from pipeline-EOR operation, oil transport, refining-fuel transport and combustion processes.

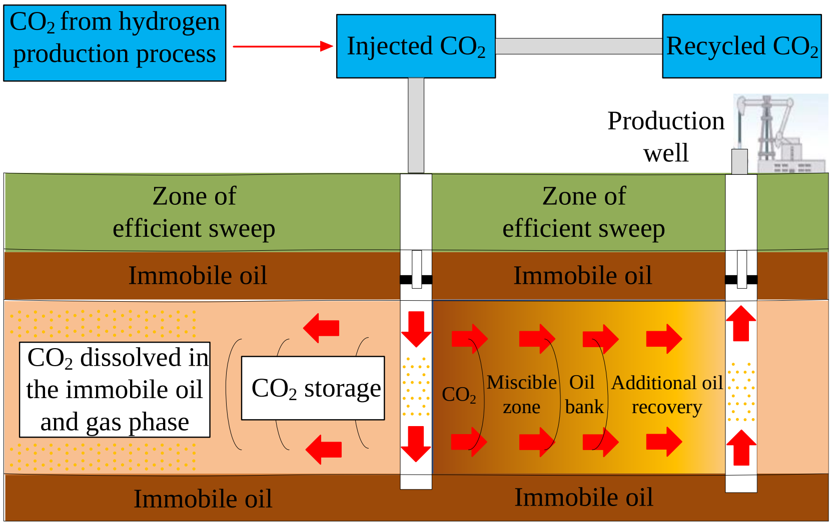

Fig. 4. General schematic diagram of EOR.

Table 5. Key information of CO_2-EOR to estimate the amount of oil produced by EOR method, the CO_2 emitted by this oil and the CO_2 that would remain sequestered.

Items	Values
Percentage of CO_2 sequestrated (%) [41]	60-70
Crude recovery ratio advanced EOR (bbl·tonneCO_2^{-1}) [42]	4.35
Emission rate of oil by CO_2-EOR (tonneCO_{2eq}·bbl^{-1}) [44]	0.1^a
CO_2 produced from conventional oil production (tonneCO_2eq·bbl^{-1}) [45]	0.0543

[a] Boundary: gate-to-gate CO_2 transport is neglected. As crude oil transport, distribution and fuel combustion apply for CO_2-EOR and conventional oil extraction, it is not considered.

[b] The amount of 9.22 gCO_2eq·MJ^{-1} LHV is equivalent to 0.543 tonneCO_2eq·bbl^{-1}. Using the LHV=43.2 MJ·kg^{-1} and a density = 0.86 kg·l^{-1} [46]. The boundary is well-to-refinery entrance gate.

The boundaries for EOR and conventional oil production are gate-to-gate because the rest of the steps e.g. oil transport, refining, and fuel combustion are the same in both cases as shown in Fig. 5. This is enough to make a comparison. Functional unit of carbon footprint for both cases is one barrel of produced oil [43].

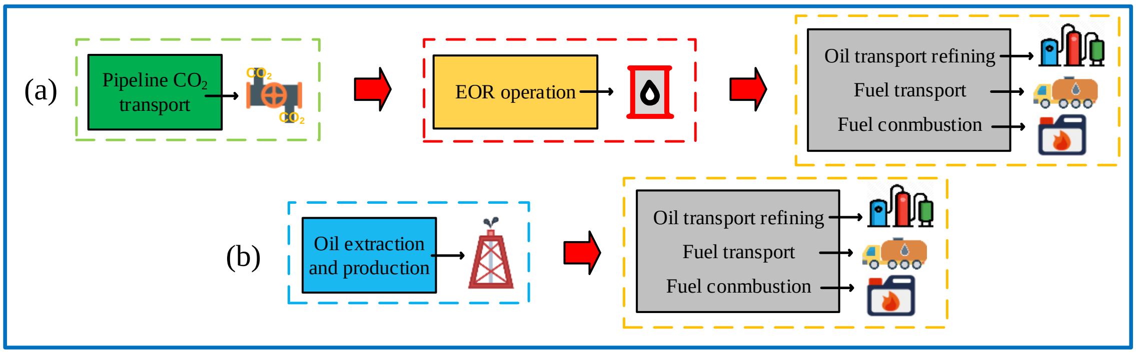

Fig. 5. Boundaries for two cases (a) CO_2-EOR; (b) conventional oil production [47].

3. Results and discussions

3.1 Technical assessment

In this section, technical results of ammonia plant and CO_2-EOR are indicated, respectively. It is developed as follows: First, results of mass and energy balance of ammonia based on 53.21 tonne·h^{-1} (1,270 tonne·day^{-1}) ammonia production are presented. The estimated amount of H_2 accounts 9.93 tonne·h^{-1}. After that, mass and energy balance of CO_2-EOR are presented based on the CO_2 generated by the ammonia plant.

3.1.1 Ammonia process

Mass balance of the main raw materials for ammonia production is shown in Table 6. It is indicated that 28.5 tonne·h^{-1} of methane is used to generate 53.2 tonne·h^{-1} of ammonia. During ammonia production process, 15 tonne·h^{-1} of CO_2 is generated. Although 90% of CO_2 is captured in the capture plant, additional fuel is burned to generate heat and steam required by the ammonia plant. Then, the overall capture rate in the ammonia plant is 77.5%. The ammonia produced is transported to the destination where H_2 is required. Then the ammonia is converted to H_2 where reaction (5) takes place.

Table 6. Mass balance of the main raw materials and ammonia production.

Components	Amount
CH_4 (tonne·h^{-1})	28.5
CH_4 additional fuel in furnace (tonne·h^{-1})	3.0
Steam (tonne·h^{-1})	96.2
H_2 to ammonia reactor (tonne·h^{-1})	10.6
N_2 (tonne·h^{-1})	47.8
Ammonia (tonne·h^{-1})	53.2
CO_2 captured (tonne·h^{-1})	66.6
CO_2 emitted (tonne·h^{-1})	15.0
CO_2 capture rate (%)	77.5

The overall efficiency of the process from SMR to ammonia reactor is 66%. The CC process is simulated in order to estimate the energy consumption and the CO_2 emission of ammonia process. The composition and mass flow rate of the syngas are presented in Table 7, which serve as the input parameters for CO_2 capture plant. The syngas flow rate is 135.2 tonne·h^{-1}, and only one post-combustion capture train is necessary to capture 95% of the CO_2. The size of the train is defined by considering a maximum of 292.5 tonne·h^{-1} approximately for the absorber column due to economic limits of absorber size. It is based on pressure drop limitation to ensure a stable operating condition with proper liquid and gas distributions [48, 49]. Table 8 presents the key results of the capture plant. The steam required to regenerate the solvent is 212 tonne·h^{-1} at 4 bar and the specific reboiler duty is 3.65 GJ·tonneCO_2^{-1}. The steam required is supplied by the same ammonia process.

Table 7. Composition and mass flow rate of the syngas to the capture plant.

Items	Values
Syngas mass flow rate (tonne·h^{-1})	135.2
CH_4 (mol %)	0.25061
H_2O (mol %)	0.62123
CO (mol %)	2.04756
H_2 (mol %)	62.4948
CO_2 (mol %)	16.5042
N_2 (mol %)	18.0394

Table 8. Summary of key parameters of the CO_2 capture (95% capture rate).

Items	Values
Syngas temperature (°C)	150
Total steam required by the capture plant (tonne·h^{-1})	212
Reboiler temperature (°C)	120
Reboiler steam pressure (bar)	4
Reboiler solvent pressure (bar)	16.5
Lean solvent mass flow rate (tonne·h^{-1})	1,494
Lean loading (molCO_2·molMEA^{-1})	0.27
Rich loading (molCO_2·molMEA^{-1})	0.457
CO_2 captured (tonne·h^{-1})	66.6
Reboiler duty (MW)	63.94
L/G ratio (mol·mol^{-1})	6.74
Specific reboiler duty (GJ·tonneCO_2^{-1})	3.65
Total PCC auxiliary power consumption (MW)	0.573

3.2 Environmental analysis

The collected CO_2 is used for EOR. However, from a life-cycle perspective, more CO_2 could be emitted. Thus the CO_2 emitted during the whole operation processes of EOR is evaluated. In order to further illustrate the advantages of the integrated processes, three case studies have been compared in Table 9 in terms of total CO_2

emission i.e. case 1: H_2 and conventional oil production, case 2: H_2 with CCS (blue H_2) and conventional oil production, and case 3: H_2 with CCU (blue H_2) and oil production via CO_2-EOR. The simplified calculation is adopted to estimate the oil production and CO_2 emission which aims to illustrate the benefit of CO_2-EOR. By using the total amount of CO_2 captured in the ammonia plant i.e. 66.7 tonne·h^{-1}, it is possible to produce 289.6 bbl·h^{-1} of incremental oil. This value is estimated based on the information presented in Table 5 [43], i.e. 4.35 barrels of oil is produced using one tonne of CO_2. As 0.1 tonneCO_{2eq} is generated per one barrel of oil produced from EOR, 289.6 bbl·h^{-1} of the oil would generate 28.96 tonne·h^{-1} of CO_2 when considering the boundary of gate to gate. The results are compared with CO_2 emitted by ammonia and conventional oil production (separated) without CCUS to identify CO_2 emission reduction of H_2 production via ammonia with CU (EOR). Although there are other implications of CO_2 emission, a simplified estimation for oil production is used to illustrate the benefit of CU. Table 10 summarises CO_2 mass balance for all case studies in terms of H_2, oil and total emission. CO_2 emission amounts of the different cases are indicated in Fig. 6. It is observed that total CO_2 emission of two processes in case 1 (81.6 tonne·h^{-1} H_2 and 15.7 tonne·h^{-1} conventional oil production) is 97.4 tonne·h^{-1}. When the CO_2 is captured and stored (case 2), CO_2 emission is reduced by 68.4% from 97.4 tonne·h^{-1} to 30.8 tonne·h^{-1} (15.0 tonne·h^{-1} H_2 and 15.7 tonne·h^{-1} conventional oil production). Finally, for the case of H_2 production with CO_2-EOR, CO_2 emission is reduced by 54.8% from 97.4 tonne·h^{-1} to 44 tonne·h^{-1} (15 tonne·h^{-1} H_2 and 29 tonne·h^{-1} from EOR). The resulting 54.8% reduction is based on the assumption that the demand of oil generated via conventional production is replaced by the oil produced via CO_2-EOR. Although the alternative with CO_2 storage demonstrates marginally higher GHG emission and cost reduction, EOR may offer the economic incentive from incremental oil production that could reduce the cost of H_2 when CCUS is incorporated, especially in developing countries e.g. Mexico and China. However, in the middle and long term, CO_2 reduction will be even more important to mitigate the climate change. Thus CO_2 storage would the most important role than CO_2-EOR.

Table 9. Comparison of three case studies of H_2 production via ammonia with and without CO_2-EOR.

Case study	Case 1	Case 2	Case 3
	H_2 without CCS + conventional oil production	H_2 with CCS + conventional oil production	H_2 with CCU: EOR

Table 10. CO_2 mass balance for three case studies.

CO_2 amount (tonne·h^{-1})	Case 1			Case 2			Case 3		
	H_2	Oil[2]	Total	H_2	Oil[2]	Total	H_2	CO_2-EOR	Total
CO_2 generated	81.6	15.7[1]		81.6	15.7[1]		81.6	29.0[1]	

CO_2 captured	66.6	0		66.6	0		66.6	0	
CO_2 storage	0	0		66.6	0			0	
CO_2 utilisation from ammonia	0	0		0	0		66.6	0	
Total CO_2 emitted	81.6	15.7	**97.4**	15.6	15.7	**30.8**	15.6	29.0	**44.0**

[1] This value is calculated considering that 66.6 tonne·h^{-1} of CO_2 will generate 190.2 bbl·h^{-1}, and each barrel of oil would generate 4.35 tonneCO_2 [42]. [2] Conventional way of oil production.

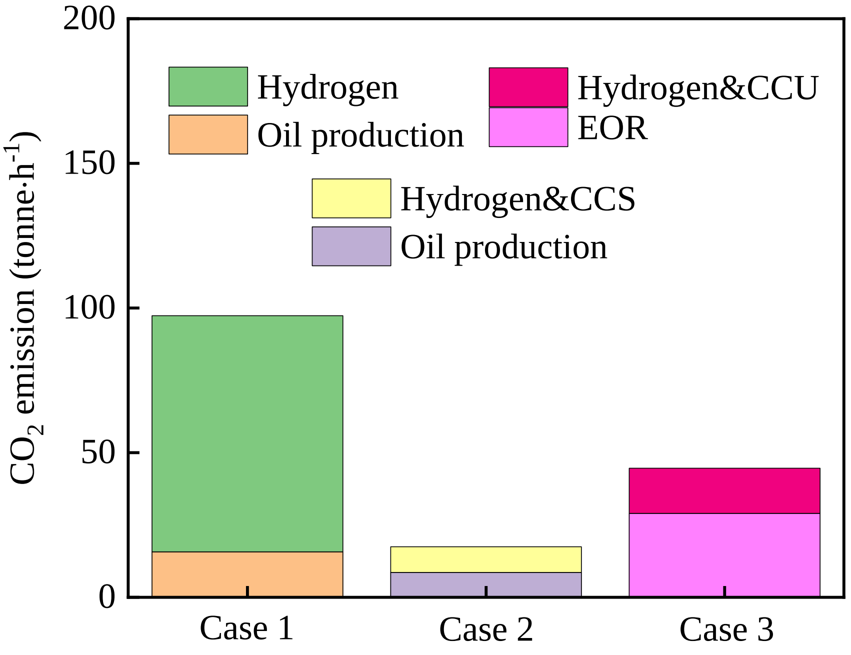

Fig. 6. CO_2 emission for: case1. Ammonia production without CCUS and conventional oil production; case 2. Ammonia production with CCS and conventional oil production; case 3. Integrated ammonia production with CCUS: oil production via CO_2-EOR.

3.3 Economic analysis

An economic analysis is carried out to quantify the cost reduction on H_2 production by transporting ammonia and the impact of the revenue for selling CO_2. The main objective of this economic study is to compare the expected cost of H_2 when taking revenues from EOR into account. The direct comparison of the expected costs of H_2 production transporting as ammonia at different fuel and CO_2 selling price is conducted by using consistent sources of information which can ensure that errors and inaccuracies in capital costs are mitigated. A sensitivity analysis is also provided to examine the robustness of the findings over a range of capital cost to account for the associated estimate uncertainties i.e. -/+ 20%.

Economic incentive is not included because it does not exist in most of the countries. Based on the entered cost of the ammonia plant with a capacity of 2,270 tonne·day^{-1} reported by Bartels [7] is 740 M$ facility in 2007.

The scaled costs are evaluated by using the chemical engineering plant cost index (CEPCI) (2017) [50], which is dimensionless and is used to adjust process plant construction costs from one period to the other. An updated cost, for instance in 2017, can be assessed by using Equation (7).

$$\mathrm{Cost}_2 = \mathrm{Cost}_1 \left(\frac{\mathrm{Index}_2}{\mathrm{Index}_1}\right) \tag{7}$$

where cost_2 is the scaled cost in 2017; Cost_1 is the cost in a base year chosen for the analysis i.e. 2011 in this analysis; Index_2 and Index_1 are the indices reported for both corresponding years i.e. 535.3 and 525.4 in 2017 and 2011, respectively.

Investment costs of the ammonia plant and the transportation are presented, which are shown in Tables 11-13. The information of the operating cost is estimated as reported by Alkusayer [27].

Table 11. Capital expenditure of the integrated processes.

Items	Values
Ammonia plant[1] (M$)	753.94
CO_2 transport[2] ($\$\cdot tCO_2^{-1}$)	3.65
CO_2 transport & storage[3] ($\$\cdot tCO_2^{-1}$)	7.25
Ammonia transportation ($\$\cdot kgH_2^{-1}$)	0.48

[1] Ammonia plant cost at 2007 [7] updated at 2017 using the chemical engineering index. [2] Cost at 2011 [51]. [3] Cost [52].

Table 12. Ammonia annual operating cost.

Type	Items	Percentage (%)	Values (M$)
Ammonia plant	Water	1.8	0.86
	Electricity	70.8	34.57
	Maintenance	11.8	5.76
	Random	1.2	0.58
	Land	0.1	0.06
	Labour	0.7	0.35
	Royalties	13.6	6.63
	Total	100	48.8[1]

[1] 33% of the total investment of the ammonia plant [27].

Table 13. Natural gas price and CO_2 selling price.

Concept	Amount	Price
Natural gas	756 ($\mathrm{tonne}\cdot d^{-1}$)	3-10 $\$\cdot \mathrm{MMBTU}^{-1}$
CO_2 captured	1598 ($\mathrm{tonne}\cdot d^{-1}$)	0-50 $\$\cdot \mathrm{tonne}^{-1}$

The estimated annual capital recovery is estimated using Equation (8), which converts the total fixed capital cost (FCI) to the value in the current year.

$$\text{Annual capital recovery} = \left[\frac{(1+i)^n - 1}{i(1+i)^n}\right] \times \mathrm{FCI} \tag{8}$$

where *i* is the interest rate and *n* is the year.

It is acknowledged that natural gas price has a significant influence on H_2 production from methane. The cost of the conventional compressed H_2 transportation is 8 €·kg^{-1} (9.05 \$·kg^{-1} at exchange rate of 1.13 at the time of writing the paper) including a dispensed hydrogen at the refuelling station [53]. The cost for transporting H_2 as conventional way via pipeline presents the high capital investment, which makes H_2 to be an expensive alternative to reduce CO_2 emission [54]. Comparably, Fig.7 shows the price at different gas price and selling CO_2 price in the case of H_2 production with CCUS and transport as ammonia. H_2 cost is estimated in terms of a range of natural gas price. Global natural gas price varies from around 3 \$·MMBTU^{-1} in North America to 8 \$·MMBTU^{-1} in Europe [55]. Due to the variation of the crude oil price for EOR projects, CO_2 sale price covers a range from 0 to \$50·tonneCO_2^{-1}. The cost of H_2 including its transportation is presented, which considers CO_2 selling price of natural gas and coal fire plants ranging \$40-50 tonne^{-1} [56, 57]. At a gas price of 10 \$·MMBTU^{-1}, H_2 cost varies from 3.78 \$·kg^{-1} to 3.46 \$·kg^{-1} when the CO_2 selling price increases from 0 to 50 \$·tonneCO_2^{-1}. At a minimum gas price of 2 \$·MMBTU^{-1}, the cost of H_2 is in the range from 2.46 \$·kg^{-1} to 2.10 \$·kg^{-1} when the CO_2 selling price increases from 0 to 50 \$·tonneCO_2^{-1}. The reduction for selling CO_2 is higher at lower gas price e.g. 8.48% and 14.63 for gas prices 10 \$·MMBTU^{-1} and 2 \$·MMBTU^{-1}, and CO_2 selling price from 0 to 50 \$·tonneCO_2^{-1}, respectively. It is demonstrated that the revenue for selling CO_2 is an opportunity to reduce CO_2 because it could accelerate the use of H_2 and the incorporation of CCUS technology in the industry.

It is evident that transporting and storage H_2 as ammonia results in low carbon economy. This process confirms that one possible barrier for H_2 produced from SMR and CCUS is the oil price. Since the oil price is very low at the time of conducting this study, the effect of the oil price increases only by 8.46% when CO_2 selling price varies from 50 \$·tonneCO_2^{-1} to 0. However, the benefit for transporting H_2 as ammonia could be observed. Also worth noting that this paper is focused on producing ammonia via SMR which could be further extended e.g. ammonia via biomass and electrolysis (mainly H_2 production) as our future work. Another possible barrier for ammonia is related to health and safety due to its low reactivity hazards for accidental combustion and explosion when compared with other fuel gases and liquids [54].

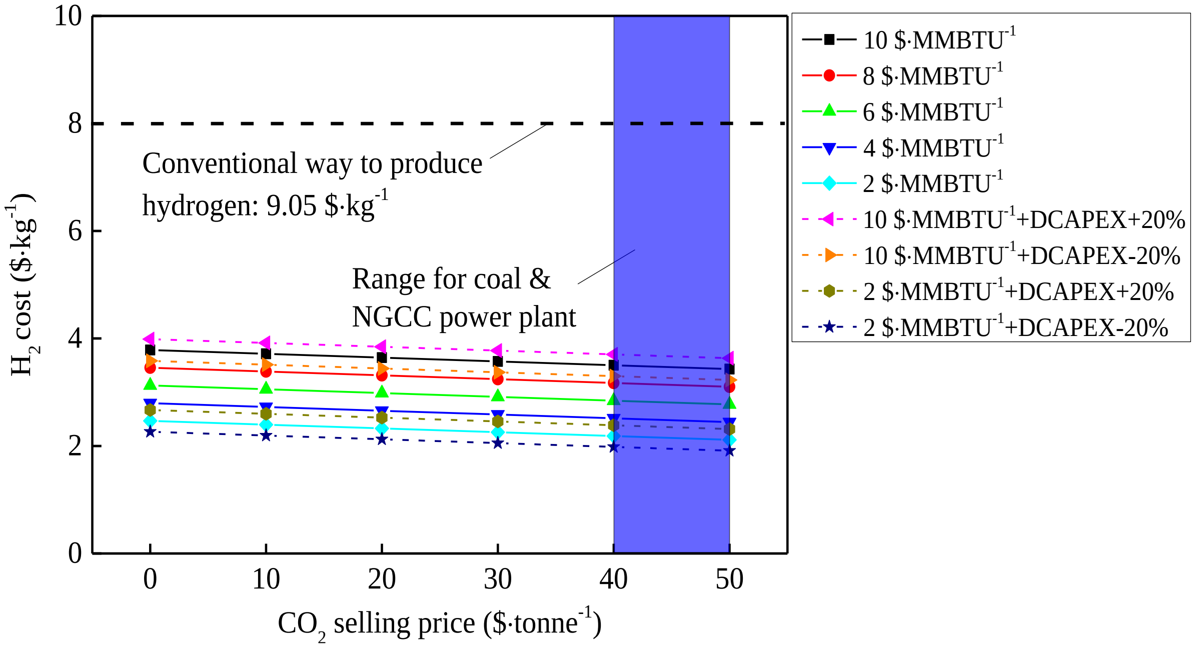

Fig. 7. H_2 cost, including its transportation as ammonia, in terms of a range of representative CO_2 price from 0 to 50 \$·tonneCO$_2^{-1}$ for EOR and natural gas prices from 2 \$·MMBTU^{-1} to 10 \$·MMBTU^{-1}. The relative variation in capital costs (DCAPEX) ranges from −20% to 20%.

4. Conclusions

In this paper, H_2 production using liquid ammonia as a carrier integrated with CO_2 storage and EOR has been assessed in term of CO_2 emission and the benefit for selling CO_2. The conclusions are yield as follows:

Compared with the alternative without CCUS, CO_2 emission could be reduced when H_2 via methane reforming is transported as the liquid ammonia and integrated with CU though it is higher than that with CCS. However, CU could lead to cost reduction. The CO_2 emission emitted for conventional oil production could be reduced from 205.6 tonne·h^{-1} to 100 tonne·h^{-1} when H_2 production is integrated with CO_2-EOR. Besides, total CO_2 emission of two separated processes i.e. H_2 and conventional oil production is 97.4 tonne·h^{-1}. When the CO_2 is captured and stored, CO_2 emission is reduced by 68.4% from 97.4 tonne·h^{-1} to 30.8 tonne·h^{-1}. For the case of H_2 production with CO_2-EOR, CO_2 emission is reduced by 54.8% from 97.4 tonne·h^{-1} to 44 tonne·h^{-1}. Moreover, a sensitivity analysis of total cost for low-carbon H_2 production process is assessed by considering the revenue for selling CO_2 for EOR in terms of a range of gas prices. At a gas price of 10 \$·MMBTU^{-1} and 2 \$·MMBTU^{-1}, H_2 costs are reduced by 9.52% and 14.63%, respectively at a CO_2 selling price from 0 to 50 \$·tonne^{-1}.

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