

#### Mitacs Accelerate Project Final Report

## Comparative assessment of NH<sub>3</sub> production and utilization in transportation systems for Ontario

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#### **SUMMARY**

In this final project report, detailed cost and feasibility analyses of selected cases are conducted. The case studies included in this report are as follows: (i) high pressure electrolysis using low cost hydropower electricity and Haber-Bosch based ammonia production; (ii) high pressure electrolysis using low cost hydropower electricity, liquefied nitrogen pumping and no main compressor Haber-Bosch based ammonia production using high pressure electrolysis via low cost hydropower electricity, liquefied nitrogen pumping, liquid nitrogen vaporization using Haber-Bosch excess heat without compressors; (iv) ammonia production using thermal plasma disassociation of methane and vaporization of high pressure liquid nitrogen via excess heat in Haber-Bosch process; (v) comparison of pumped hydro storage and ammonia production using excess power; (vi) wind based electrolysis based ammonia production with Haber-Bosch process; (vii) nuclear high temperature electrolysis based ammonia production options.

The results of this project report indicates that the compression cost of hydrogen to about 20 bar corresponds to 1.03 \$/kg H<sub>2</sub> which constitutes approximately 15% of the overall hydrogen production cost. Therefore, high pressure water electrolysis system is an alternative option for reducing the required power of ammonia synthesis process by eliminating the main compressors in the ammonia synthesis process. Utilizing high pressure PEM electrolyzers have the capability to reduce hydrogen production cost about 0.40 \$/kg compared to mechanical compression. Using pressurized water require less power than using hydrogen compressor which decreases the required power. The lowest cost of high pressure electrolysis based ammonia production is calculated to be 0.76 US \$/kg for 3.5 US cent/kWh electricity price.

Thermal plasma disassociation of methane is an alternative option for ammonia production which brings approximately 20% less power input. When carbon black sales are considered, the cost of ammonia can decrease down to 0.42 \$/kg which is quite lower than other methods. However, the process of liquefied natural gas production and the effect of high pressure need to be analyzed in detail in order to assess the overall performance.

At present, the average ammonia selling price is about 770 US\$/ton in the USA. In the case where the ammonia production cost was achieved under 700 US\$/ton, the pumped hydro storage plant yearly profit would be nearly same with a 300 ton/day ammonia production plant profit with a power requirement of 145 MW. However, the capital installation cost of pumped storage hydro plant becomes nearly twice of ammonia plant.

Nuclear based ammonia production options are cost competitive than other methods however the initial investment costs are much higher. The high capital costs are the major disadvantage of nuclear powered ammonia production however, by enabling smaller and standardized modular reactors, it could reduce the capital costs, construction cost and time, licensing cost and time. Developed Haber-Bosch technology would be optimized using liquid pumping instead of feed gases compression, high pressure electrolysis and liquid nitrogen and LNG vaporization via excess heat of Haber-Bosch reactor.

Furthermore, the previously completed progress reports are appended to this current report.

#### I. FEASIBILITY ANALYSIS

In this section, the feasibility analysis of high pressure electrolysis, Haber-Bosch process, cryogenic air separation, ammonia synthesis loop are conducted and the total investment costs are comparatively assessed.

#### 1. Feasibility analysis of high-pressure electrolysis based ammonia production

In high temperature electrolysis process, the modification to a normal proton exchange membrane electrolyzer is that instead of having an atmospheric pressure hydrogen as end product, compressed hydrogen is produced between 120–200 bar at 70°C-120°C. Therefore, by pressurizing the hydrogen in the electrolyzer instead of pressurizing in the compressor, the necessity for an external hydrogen compressor is eliminated. The advantages and disadvantages of high pressure PEM electrolysis can be listed as in Table 1.

Advantages	Disadvantages
Elimination of multiple stage mechanical compression.	Loss of stack seals and membrane extrusion into fluid ports
Decrease in complexity of the system.	Need of improved strength without effecting conductivity
Lower drying requirement	Increasing membrane degradation with operating pressure
Less maintenance requirement	Important growth in chemical degradation rate under high pressure operation
No moving parts	Low resistance because of thin membranes, allowing efficient operation at high current densities.
No contaminants	Similar faradaic losses in PEM fuel cells and electrochemical hydrogen compressors under same operating conditions and membrane selection
Flexibility of hydrogen production at end user site	High back diffusion

Table 1	. The	advantages	and disa	advantages	of high	pressure PEM	electrolvsis
					D		

Source: Data from Ref. [1].

Although there are some drawbacks of high pressure PEM electrolysis systems, together with the improvements, the advantages in cost reduction makes this technology promising for the near future hydrogen production options.



Fig. 1. Electrolysis based hydrogen production and delivery cost contribution from different processes in \$/kg (data from Ref. [1])

As it can be seen in Fig. 1, delivery cost of hydrogen after production constitutes approximately 38 % of the overall cost. Delivery does not only include transmission but also compression of the hydrogen after production at standard pressures. The detailed cost distribution of delivery process for hydrogen is illustrated in Fig. 2. The compression cost of hydrogen to about 20 bar is 1.03\$/kg which corresponds to 15% of the overall cost. The DOE Forecourt H2A Model (Ver. 3.0) was used to project the cost of hydrogen production with the high pressure electrolysis technology. Tradeoffs of operating pressure, system efficiency and capital costs were conducted using a standard set of assumptions and cost parameters. The cost of electricity is considered as US\$0.061/kWh [1, 2].



Fig. 2. Hydrogen compression and delivery cost contribution from different sub-processes in \$/kg (data from Ref. [1])



Fig. 3. Cost of compression in high pressure PEM electrolyzer (data from Ref. [1])

Fig. 3 and Table 2 show that if high pressure electrolyzer is used at 432 bar, the compression cost decreases to 0.31 US\$/kg but feedstock cost increase becomes 0.31 US\$/kg. The cost of electricity is considered as US\$0.061/kWh. As mentioned previously, The DOE Forecourt H2A Model was used for the cost calculations.

Pressure (bar)	Compression Cost (\$/kg)	Additional Feedstock Cost (\$/kg)	Total Cost (\$/kg)
21	1.03	0	1.03
431	0.31	0.31	0.62
874	0.12	0.49	0.61

Table 2. Cost comparison of using compressors or high pressure electrolyzers

Source: Data from Ref. [1]

The cost of electricity is considered as US\$0.061/kWh for this comparison. As seen in above Fig. 3 and Table 2, there is about US\$0.40 (40%) cost reduction compared to mechanical compression when high pressure PEM electrolyzer is utilized.

A differential pressure PEM electrolysis system consists of a number of bipolar cells stacked in electrical series, with each cell containing a membrane-electrode assembly (MEA) formed by bonding anode and cathode electrodes to opposing sides of the membrane. The MEA is in contact with electrically conductive anode and cathode support structures located in the oxygen and hydrogen chambers, respectively. An electrically conductive cell separator is located between the anode and cathode chambers of adjacent cells. In the process, high-purity water is pumped to the anode, where it is electrochemically decomposed to oxygen gas, hydrogen ions and electrons. The hydrogen ions move through the PEM and the electrons move through the external circuit to the cathode, where they recombine to form hydrogen. An excess of water is supplied to

the oxygen side of the cell and is recirculated to remove waste heat from the MEA. A portion of the excess water is electro-osmotically transported across the PEM with the hydrogen ions. The electrochemically-transported water is separated from the product hydrogen and returned to the water stream. PEM cells operate efficiently at current densities of 2000 to 3000 mA/cm<sup>2</sup>, compared to alkaline electrolyzers that typically operate at less than 300 mA/cm<sup>2</sup>. At this current density, the alkaline cell voltage is typically 1.9 V or higher. The operating cell voltage of the currently analyzed 15-kW PEM electrolyzer is lower, 1.85 V, at a current density nearly an order of magnitude higher, 2000 mA/cm<sup>2</sup> at 300 psig (2170 kPa) H<sub>2</sub>. In the study, the electrolyzer demonstrated a PEM electrolysis cell based on an advanced membrane that operates at 1.7 V at 2000 mA/cm<sup>2</sup>. Since the cost of electricity is the major contributor to the cost of hydrogen produced by electrolysis, efficient operation is a key to low-cost hydrogen production for large applications. Although the capital cost of PEM electrolyzer stacks is higher than that of alkaline stacks on an area basis, the much higher current density of PEM cells allows the stacks to be smaller by a factor of 5 to 10, while achieving high efficiency. Thus, in large-scale production, and with development of lower-cost materials and manufacturing methods for key components, the capital cost of a PEM stack is expected to be competitive with alkaline stacks, while the electricity consumption of the PEM stack will be significantly lower than that of the alkaline stack. Another key advantage of the PEM technology is the ability to operate the stack at a high differential pressure, allowing hydrogen to be produced at high pressure, while oxygen is produced, and the reactant water is supplied, at near atmospheric pressure. Production of hydrogen in the electrolyzer at elevated pressure provides some system advantages, decreasing the number of stages of mechanical compression required to store the product hydrogen at greater than 5000 psig (34.6 MPa) [2].

The price for electrolyzer with electrochemical and mechanical compression seems to be similar at large scale production [3]. Price advantage for electrochemical compression may be obtained at decentralized energy supply for < 1 MW [3]. High pressure hydrogen electrolysis at present time may be efficient or reasonable from economic point of view up to operating pressure 200-300 bar [3]. Electrochemical compression of hydrogen creates problems with gas purity, current efficiency, platinum metals loading and life-time mainly at often turn off - turn on cycles [3]. The change in current efficiency with varying pressure values in PEM electrolyzer are given in Fig. 4. If the pressure increases, current efficiency tends to decrease. The conditions in the Fig. 4 were: current density is 1000 mA/cm<sup>2</sup>, operating voltage is 1.70-1.73 V and operating temperature is 80 °C with a modified membrane of 250 micrometers.



Fig. 4. Pressure vs current efficiency in PEM electrolyzer under given conditions (data from Ref. [3])

High pressure hydrogen could be generated by using compressor which will deliver hydrogen from 1 atm to higher pressure, or using pump to supply pressurized water. Using pump instead of compressor requires less power than compressor [4]. Therefore, the current industry trend is to greatly pressurized electrolyzers to abolish classical mechanical compressors for efficiency enhancement. When the efficiency of the compressor and the pump are assumed to be 50%, it is realized that hydrogen produced by using pressurized water require less power than using hydrogen compressor. The required power difference is about 15% which is a significant amount. The advantage of using pressurized water via pump instead of power consuming compressor was demonstrated as seen in Figs. 5 and 6.



----- Linear (Electrolyzer and Pump Work (kW))



Fig. 5. Comparison of high pressure electrolysis and atmospheric electrolysis required work inputs (data from Ref. [5])



Fig. 6. Energy use of a solid polymer electrolyzer at different temperature and pressure values (data from Ref. [5])

Fig. 6 represents the increase in power consumption of a PEM electrolyzer when the pressure increases. However, rising temperature has positive effect on efficiency yielding lower power consumption. The electrolyzer consumes about 46 kWh/kg H<sub>2</sub> energy at 100 bar and 320 K while the energy consumption goes down to about 38 kWh/kg H<sub>2</sub> at same temperature and 523 K. Therefore, rising the temperature positively affect the electrolysis efficiency where high temperature and high pressure electrolysis can be combined.

The following assumption are made for the cost calculations of electrolysis, transportation, storage and production systems in the next section as given in Ref. [6, 7]:

- The H2A Distributed Production Model 3.0 used alkaline electrolysis parameters to generate the values.
- The H2A Distributed Production Model 3.0 was used with the standard economic assumptions: all values are in 2007 dollars, 1.9% inflation rate, 10% after tax real internal rate of return, 100% equity financing, 20-year analysis period, 38.9% overall tax rate, and 1% working capital. The plant design capacity is 1,500 kg/day of hydrogen. It is assumed that Design for Manufacture and Assembly (DFMA) would be employed and that production would have realized economies of scale.
- The plant production equipment availability is 98% including both planned and unplanned outages; four unplanned outages of 14h duration per year; 1 planned outage of 5 days duration per year. The plant usage factor is defined as the actual yearly production/equipment design production capacity and is 90% based on over sizing of the production equipment to accommodate a summer surge in demand of 10% above the yearly average demand.
- The levelized cost is equivalent to the minimum required selling price to achieve a 10% annual rate of return over the life of the plant.
- Electrolyzer cells capital replacement is 25% of total purchased capital every 7 years
- The 2015 status of transmission pressure is based on the maximum operating pressure of hydrogen pipelines as of March 2015. The 2020 target is set to lower compression requirements at the forecourt.
- Hydrogen leakage is hydrogen that permeates or leaks from fittings, etc., as a percent of the amount of hydrogen carried by the pipeline. The 2015 status and future targets are based on industry consultation, along with the assumption that leak rates from hydrogen pipelines will be no higher than those from current natural gas pipeline infrastructure.
- Pipeline lifetime refers to the minimum time period that the pipeline must remain in service to justify the capital cost of its installation. The 2020 and ultimate targets are intended to be at least equivalent to that of natural gas pipeline infrastructure. The actual life of a pipeline can exceed its design life.
- The leak rate refers to hydrogen losses through the pipeline material and/or fittings. The current status and future targets are based on the use of fiber-reinforced composite piping (FRP).
- Tube trailer terminals large enough to serve a mature market (~ 70,000 kg/day) do not presently exist. Such terminals would likely be located near production plants and require storage capacity (at about 100 bar) to buffer differences between production rates and rates of trailer filling. The compressors in 2015 do not seem to have sufficient capacity to meet the needs of a terminal in a mature market. The 2020 target is based on the capacity that would be necessary to satisfy the truck refueling needs of a terminal in a mature market with about 20 compressors in parallel and 5 redundant compressors.



Fig. 7. Pipeline, terminal and geologic compressors based hydrogen transportation (adapted from Ref. [6])

In general, geological storage is typically employed to store a large amount of gas in the field of infrastructure for supplying natural gas 150-200 bar pressure medium. In order to reduce the gas loss, usually salt domes are used forming a cavity. One has been operating for several years, two more are recently built in Texas, the United States of America, Lake Jackson, Texas, as a salt cave site hydrogen storage. Demand for road transport fuel will be significantly higher in summer than in winter. In the summer the cost of the ban, there is the potential to meet this growing demand, by hydrogen storage capacity of hydrogen in the fuel system. Geological type storage is very cost-effective way, and the effective use of natural gas is also possible [6].

Note that the compression process may vary according to the capacity and use of pressurization. Transport pipelines, high flow rate of at least 10 MPa, at a relatively low pressure and compression ratio (10: 1) are required. On the other hand, at fueling stations, flow compressors 5-100 kg/h and the pressure can be as high as 100 MPa. Installation of terminals tend to have temporary needs. High flow rate of reciprocating compressors are often used to transport pipelines and terminals used for excitation of the hydrogen cell pressure vessel installation and high-pressure diaphragm compressors. The pipeline, terminal and geologic compressors based hydrogen transportation and the related cost analysis are given in Fig. 7 and Table 3.

Category	2015	2020
Compressor specific energy (kWh/kg)	0.82	0.82
Discharge pressure (bar)	100	100
Uninstalled capital cost (million \$)	5.5	3.6
Availability	85%	90%
Annual maintenance cost (% of installed capital cost)	6%	4%
ourse: Data from Paf [6]		

Table 3. Hydrogen delivery components cost analysis for pipeline, terminal and geologic compressors for 200,000 kg/day hydrogen capacity and 20 bar inlet pressure (estimated)

Source: Data from Ref. [6]

The pipeline capital costs are from HDSAM (Hydrogen delivery scenario analysis model) V2.3 prepared by US DOE. The model assumes that a hydrogen pipeline costs 10% more to construct than a natural gas pipeline of the same diameter and length. The assumption of a 10% premium for hydrogen lines was based on discussions with industrial gas companies that build and operate the current system of hydrogen pipelines in the U.S [6, 7]. The 2015 status and future targets are based on distribution pipelines being built out of fiber-reinforced composite material. The 2015 distribution pressure is based on the current rating of fiber-reinforced composite pipe.

The ultimate target has been set to enable the pipeline delivery pathway to meet its ultimate cost target.



Fig. 8. Tube trailer based hydrogen transportation system (adapted from Ref. [6])

Pipelines carrying large volumes for hydrogen perceived cost-effective way. Because of the high capital investment for pipelines, however, there must be a steady, high-volume gas demand to justify the investment cost. Distribution line pressure of 1-5 MPa (10-50 bar), while the transmission line pressures are generally in the range of 3-15 MPa (30-150 bar) are available. Materials are soft and low carbon steels. Embrittlement concerns for these materials are far less than for higher strength steels and are further mitigated by proper pipeline design. Long pipelines for liquid hydrogen are currently cost prohibitive.

The compressor specific energy is calculated by energy consumption for every unit of hydrogen compressed (kWh/kg) at the specified inlet pressures, discharge pressures, and capacities. The current metric characterizes the isentropic efficiency, losses, motor efficiency, and motor size of a large compressor. Large compressor capital costs were derived from cost data supplied by various vendors for two- and three-stage reciprocating compressors. HDSAM V2.3 had been used to estimate the motor power that a reciprocating compressor of the specified size (200,000 kg/day from 20 bar to 100 bar) would require, and to then estimate the compressor cost corresponding to that power. The 2015 status is instead based on cost projections for an existing centrifugal design, which is likely to be preferable to reciprocating compression because of better reliability. The 2020 and ultimate targets are based on cost reductions. Hydrogen can leak through compressor seals. The 2015 status of leak rate was based on typical ratings of hydrogen compressor seals. Future targets are set to ensure leak rates do not exceed the current status. Annual maintenance cost status was derived from a reliability analysis completed by Concepts NREC for the 240,000 kg/day centrifugal compressor which is about \$0.005/kWh. HDSAM V2.3 was used to determine the kWh the compressor would consume in a year [6, 7].

Category	2015	2020
Compressor specific energy (kWh/kg)	1.1	1.1
Capacity (kg/h)	40	300
Discharge pressure (bar)	550	550
Uninstalled capital cost (\$)	250,000	450,000
Availability	90%	90%
Annual maintenance cost (% of installed capital cost)	10%	2%
Source: Data from Ref. [6]		

Table 4. Tube trailer terminal truck refueling compressors cost analysis for 300 kg/h hydrogen capacity and 100 bar inlet pressure (estimated)

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The tube trailer based hydrogen transportation system and their cost analysis are given in Table 4 and Fig.8. The individual component targets for 2020 have been set such that the tube trailer delivery pathway meets the cost target of \$2.00/gge of hydrogen. The ultimate targets have been set such that the pipeline delivery and liquid hydrogen delivery pathways both achieve a cost of <\$2.00/gge. Ultimate targets were not set for the tube trailer pathway because it is expected that gaseous hydrogen will be delivered primarily by pipelines in a mature, high-volume market. The most common pressure vessel construction is the Type 1 steel tube. These are capable with a storage capacity of gaseous hydrogen under a pressure of 13.5 41 MPa (135-410 bar) and bonded together to increase the overall storage capacity. Storage pressure vessels, ships carrying container depends on the size and construction design is based on the regulations. Current carrying capacity of steel pipe trailer (~ 18 MPa or 180 bar) hydrogen is limited. Because of the limited amount of hydrogen that can be transported by steel tube trailer, this transport approach is economically constrained to a radius of ~300 km from the point of production. Hydrogen gas delivery can be with the railway or may be provided with vessels and barges. Composite pressure vessels are also available. Typically these cost more than steel vessels of equivalent size, but generally will store hydrogen at higher pressures and capacity, and storage costs on per kg of hydrogen stored basis are often lower [6, 7].

Table 5. Costs of stationary hydrogen gas s	Table 5. Costs of stationary hydrogen gas storage tanks (estimated)			
	2015	2020		
Stationary hydrogen gas storage tanks	(\$/kg hydrogen	(\$/kg hydrogen		
	stored)	stored)		
Purchased capital cost for low pressure 160 bar	850	500		
Purchased capital cost for moderate pressure 430 bar	1,100	600		
Purchased capital cost for high pressure 925 bar	2,000	600		

Table 5 Costs of stationary hydrogen and storage tanks (astimated)

Source: Data from Ref. [6]

If the hydrogen is produced at the required purity specifications, then design of the delivery infrastructure must either guard against contamination or provide for a final purification step just prior to dispensing. Alternatively, hydrogen could be produced at lower purity levels and purified to specification further downstream along the delivery pathway prior to dispensing. Purchased capital costs of stationary hydrogen gas storage tanks are given in Table 5.

Table 6. Distributed	forecourt water	electrolysis	hydrogen	production (	(estimated)	,
	101000uit muter	0100019515	nyarogen	production	(obtilinated)	

Characteristics	2015	2020
Hydrogen Levelized Cost (Production Only) (\$/kg)	3.9	2.3
Electrolyzer System Capital Cost (\$/kg)	0.5	0.5
System Energy Efficiency (%)	72	75
System Energy Consumption (kWh/kg)	46	44
Stack Energy Efficiency (%)	76	77
Stack Energy Consumption (kWh/kg)	44	43
Source: Data from Ref [6]		

Source: Data from Ref. [6]

These individual targets were based on the current status of the technology and the potential for technological advancements in the future. The status of these technologies was determined through consultations with stakeholders and industry [6, 7]. The cost contributions of various processes in distributed water electrolysis based hydrogen production system are given in Tables 6 and 7. Costs for the forecourt station compression and storage are consistent. Storage capacity for 1579 kg of hydrogen at the forecourt is included. It is assumed that the hydrogen refueling fill pressure is 10,000 psi in 2015 and 2020. The comparison of stationary hydrogen tanks under various pressures is given in Fig. 9 based on \$/kg price.



Purchased Capital Cost of Hydrogen Storage Tanks (\$/kg hydrogen stored)

Fig. 9. Comparison of costs for stationary hydrogen gas storage tanks (data from Ref. [6])

As indicated in Fig. 9, various effective pressures are likely for stationary storage purposes in a hydrogen delivery infrastructure. Low pressure storage will be necessary at terminals and fueling stations supplied by pipelines. Moderate pressure storage will be necessary at 350 bar refueling stations, and high-pressure storage will be necessary at 700 bar refueling stations. The 2015 values represent the packaged cost of standard steel and composite tanks, including the costs of paint, cleaning, and mounting necessary to transport the tanks; this cost does not, however, include installation at the final destination. Because the cost of storage is highly dependent on the tank size. The ultimate target for tank size is smaller in order to create a more aggressive target on a \$/kg stored basis [6, 7].

Table 7. Distributed electrolysis cost contributions (est	mateu)	
Characteristics	2015	2020
Electrolysis System (\$/kg hydrogen)	0.5	0.5
Electricity (\$/kg hydrogen)	3.1	1.6
Production Fixed O&M (\$/kg hydrogen)	0.2	0.2
Production Other Variable Costs (\$/kg hydrogen)	0.1	< 0.10
Hydrogen Production (\$/kg hydrogen)	3.9	2.3
Compression, Storage, and Dispensing (\$/kg hydrogen)	1.7	1.7
Total Hydrogen Levelized Cost (Dispensed) (\$/kg hydrogen)	5.6	4
Source: Data from Ref. [7]		

 Table 7. Distributed electrolysis cost contributions (estimated)

The electricity cost is assumed to be 3.7¢/kWh for the year 2020 only. Distributed electrolysis based hydrogen production cost contributions are given in Fig. 10. Furthermore, the central water electrolysis in high amounts yield lower costs as seen in Table 8 and Table 9. The cost of central electrolysis based hydrogen can decrease down to 3.2 \$/kg as illustrated in Fig. 11.





Fig. 10. Distributed electrolysis cost contributions (estimated) (data from Ref. [7])

Note that system energy efficiency is defined as the energy in the hydrogen produced by the system on a LHV basis divided by the sum of the feedstock energy as LHV plus all other energy used in the process. Stack energy efficiency is defined as the energy in the hydrogen produced by the stack on a LHV basis divided by the electricity entering the stack. Additional electricity use for the balance of plant is not included in this calculation. Hydrogen cost is calculated assuming purchase of industrial grid electricity. The average electricity price is taken to be \$0.070/kWh (\$0.069/kWh effective).

	(	
Characteristics	2015	2020
Hydrogen Levelized Cost (Plant Gate) (\$/kg)	3.2	2
Total Capital Investment (\$M)	51	40
System Energy Efficiency (%)	73	75
System Energy Consumption (kWh/kg)	46	44.7
Stack Energy Efficiency (%)	76	78
Stack Energy Consumption (kWh/kg)	45	44
Electricity Price	0.05	0.03

Table 8. Central water electrolysis hydrogen production (estimated)

Source: Data from Ref. [7]

The H2A Distributed Production Model 3.0 was used with the standard economic assumptions: all values are in 2007 US dollars, 1.9% inflation rate, 10% after tax real internal rate of return, 100% equity financing, 20-year analysis period, 38.9% overall tax rate, and 1% working capital. The plant design capacity is 1,500 kg/day of hydrogen. It is assumed that Design for Manufacture and Assembly (DFMA) would be employed and that production would have realized economies of scale.

Table 9. Central water electronysis cost contribution	is (Csun	lateu)
Characteristics	2015	2020
Capital cost (\$/kg)	0.5	0.4
Feedstock cost (\$/kg)	2.3	1.4
Fixed O&M cost (\$/kg)	0.1	0.1
Other variable costs (\$/kg)	0.1	0.1
Total Hydrogen Levelized Cost (Plant Gate) (\$/kg)	3.2	2
Source: Data from Ref. [7]		

Table 9. Central water electrolysis cost contributions (estimated)

The plant production equipment availability is 98% including both planned and unplanned outages; four unplanned outages of 14h duration per year; 1 planned outage of 5 days duration per year. The plant usage factor is defined as the actual yearly production/equipment design production capacity and is 90% based on over sizing of the production equipment to accommodate a summer surge in demand of 10% above the yearly average demand. The levelized cost is equivalent to the minimum required selling price to achieve a 10% annual rate of return over the life of the plant. The electrolyzer cells capital replacement is 25% of total purchased capital every 7 years [7].



±2015 II 2020

Fig. 11. Central water electrolysis cost contributions (estimated) (data from Ref. [7])



Fig. 12. Average electricity prices for large power consumers higher than 5 MW in North America in Canadian cent/kWh (adapted from Ref. [8])

The electricity rates effective April 1, 2015 sets out Hydro-Québec's rates, as approved by the Québec energy board in accordance with Decision D-2015-033. Taxes are not included in the calculations. These bills have been estimated by Hydro-Québec and may differ from actual bills. The electricity prices in the tables and figures are based on Canadian dollars [7].



Fig. 13. Comparative index of electricity prices for large-power customers with a monthly consumption of 3,060,000 kWh and a power demand of 5,000 kW (data from Ref. [8])

The results presented in Fig. 13 and Table 10 show the total bill for various consumption levels. If the bill is calculated according to an unbundled rate, it includes all components, including supply, transmission and distribution. The electricity prices in Canada are given in Fig. 13 and Table 10 in Canadian dollar. The lowest electricity cost is calculated for Winnipeg.

Power demand	5 MW	5 MW	10 MW	30 MW	50 MW	50 MW
Load factor	0.65	0.85	0.80	0.81	0.65	0.85
		]	Price (CA	D cent/kV	Vh)	
Montreal, QC	5.76	5.17	5	4.97	5.4	4.9
Calgary, AB	5.04	4.76	4.8	4.78	5.01	4.74
Charlottetown, PE	9.63	8.9	9.05	9.01	9.63	8.9
Edmonton, AB	7.61	6.97	4.47	4.32	4.57	4.22
Halifax, NS	10.66	10.02	10.15	10.12	10.66	10.02
Moncton, NB	8.24	7.48	7.27	7.24	7.81	7.14
Ottawa, ON	9.87	9.3	10.31	6.9	6.83	6.13
Regina, SK	8.36	7.81	6.72	6.63	6.94	6.55
St. John's, NL	8.93	8.65	8.61	4.82	5.1	4.77
Toronto, ON	9.28	9.22	5.7	5.64	6.05	5.55
Vancouver, BC	7.58	7.04	5.93	5.91	6.25	5.84
Winnipeg, MB	5.08	4.67	4.08	4.07	4.33	4.02

Table 10. Large power average electricity prices effective on April 1, 2015 in CAD cent/kWh

Source: Data from Ref. [8]

## 1.1 Economic analysis of high pressure PEM electrolyzer based hydrogen and ammonia production

The DOE H2A model was used to project the cost of hydrogen production with the high pressure electrolysis technology and to determine the lowest cost system design. The costs are given in US dollars in this section. The H2A model was run for production of 1500 kg  $H_2$ /day at a forecourt filling station.

The capital and operating costs include a compressor for increasing the hydrogen pressure from the stack operating pressure to the DOE target storage pressure of 6250 psig (43.2 MPa). The cost of hydrogen produced using the high pressure PEM electrolysis technology was analyzed as a function of four operating pressures, ranging from 100 psig (0.79 MPa) to 5000 psig (34.6 MPa), and three current densities: 1000, 2000 and 3000 A/ft<sup>2</sup> (929, 1858 and 2787 mA/cm<sup>2</sup>, respectively). Analysis was conducted for two electricity rates: (i) 0.05/kWh for industrial electricity where the results are shown in Table 11; and (ii) a lower cost of 0.035/kWh. Where the results are shown in Table 12. At the higher electricity cost (0.05/kWh), the lowest projected cost for hydrogen production is 3.77/kg, for an electrolyzer designed to operate at 100 psig (0.79 MPa) and a moderate current density of 1858 mA/cm<sup>2</sup> [2].

Pressure (bar)	Current density (mA/cm <sup>2</sup> )	Cell voltage (V)	Cell power consumption (kWh/kg H2)	Stack Projected Capital Costs(\$K)	Compressor Capital Costs(SK)	Total Projected Capital Costs(\$K)	H <sub>2</sub> cost(\$/kg) Capital	H <sub>2</sub> cost(\$/kg) Electricity	H <sub>2</sub> cost(\$/kg) O&M	H <sub>2</sub> cost(\$/kg) Total
345	929	1.807	52.9	2204	0	5050	2.23	3.02	0.86	5.95
345	1858	2.016	52.9	1054	0	3085	1.37	3.26	0.59	5.06
345	2787	2.218	61.2	691	0	2474	1.1	3.56	0.51	5.01

 Table 11. Cost of hydrogen for high pressure electrolysis based on electricity price of 5

 cents/kWh

Source: Data from Ref. [2]

Table 12. Cost of hydrogen for high pressure electrolysis based on electricity price of 3.5 cents/kWh

Pressure (bar)	Current density (mA/cm <sup>2</sup> )	Cell voltage (V)	Cell power consumption (kWh/kg H <sub>2</sub> )	Stack Projected Capital Costs(\$K)	Compressor Capital Costs(SK)	Total Projected Capital Costs(\$K)	H2 cost(\$/kg) Capital	H <sub>2</sub> cost(\$/kg) Electricity	H2 cost(\$/kg) O&M	H2 cost(\$/kg) Total
345	929	1.80	52.9	2204	0	5050	2.2	2.01	0.86	4.92
345	1858	2.01	52.9	1054	0	3085	1.3	2.17	0.59	3.95
345	2787	2.28	61.2	691	0	2474	1.0	2.37	0.51	3.8

Source: Data from Ref. [2]



Fig. 14. Cost comparison of hydrogen production from high pressure PEM electrolysis based on various electricity price and current densities at 345 bar (data from Ref. [2])

The projected cost of hydrogen increases with increasing stack and system operating pressure. For an electrolyzer stack producing hydrogen at 5000 psig (34.6 MPa), the lowest projected hydrogen cost is approximately \$5.00/kg, a 25% increase over the 333-psig (2.4 MPa) case. Higher pressure operation reduces the compressor costs, but significantly increases the capital cost of the electrolyzer stack and system. This is particularly true for operation at 5000 psig (34.6 MPa), where the high pressure limits the practical size (active area) of the individual cells and reinforced sealing is required for each cell.

As the results shown in Fig. 14, the larger number of cells and the higher cost per cell, as well as a higher cost for the balance-of-plant components rated for 5000-psig (34.6 MPa) operation, result in a significantly higher capital cost for the 5000-psig (34.6 MPa) electrolyzer compared to lower pressure designs. The estimated cost of the present stack design in large-scale production is less than \$1000/kW. A future development path has been identified that would decrease the capital cost to less than \$550/kW. Economic analysis indicates that hydrogen could be produced for \$3.79 per gge at an electricity cost of \$0.05/kWh by the lower-cost PEM electrolyzer assuming high-volume production of large-scale electrolyzer systems [2].

## 2. Feasibility analysis of cryogenic air separation for nitrogen production in ammonia synthesis

Cryogenic air separation methods are regularly used in medium to large scale facilities to yield nitrogen, oxygen, and argon as gases or liquid products. Cryogenic air separation is generally favored technology for generating very high purity oxygen and nitrogen. Currently, it yields the most cost effective technology for high amounts. There are numerous plants producing liquefied industrial gas products using cryogenic technology.

The plants which produce nitrogen only are less complicated and need less power to operate than an oxygen-only plant making the same amount of product. Producing these products in liquid form requires extra apparatus and more than doubles the amount of power required per unit of delivered product [9].

If a high percentage of facility produces liquid products, an additional refrigeration element must be added to a standard air separation plant (ASU). These units are called liquefiers and they use nitrogen as the primary working fluid. The needed liquefier volume is decided by considering the estimated average daily demand for bulk liquid products and the need to produce some additional liquid to back up on-site gas customers served out of the same air separation plant [9].

If the liquefier is being added to an existing ASU, the ASU may not have been designed to allow high rates of liquid oxygen withdrawal. In this case, one solution is to add extra heat exchanger circuit to liquefy gaseous oxygen while vaporizing liquid nitrogen. Refrigeration is transmitted to the air separation section of the plant via heat exchangers and injection of liquid nitrogen as distillation column reflux [9].

The general process design of a cryogenic air separation plant involves the following steps:

- Air is compressed and cooled with intercoolers to remove any water vapor
- The dry air stream is purified to remove contaminants such as carbon dioxide and residual water vapor
- The air is cooled using the waste product oxygen and purified nitrogen from the distillation column, further deducing contaminants
- The air is further cooled down to about 97 K (the dew point of air)
- The air is distilled into its components using a single distillation column

The cost of reciprocating compressors is proportional to plant capacity while the cost of centrifugal compressors varies very little over a wide range of large plant sizes [10]. Therefore, when centrifugal compressors were first introduced, the threshold for switching from reciprocating compressors to centrifugal compressors was estimated to be between 550 and 600 ton/day [10]. Today with improved manufacturing techniques, improved catalysts and lower synthesis pressures in some plants, centrifugal compressors are economical down to 220 ton/day [11].

Nearly all contemporary ammonia plants use centrifugal compressors for syngas compression, though reciprocating compressors were used until the mid-1960s. The compressors utilize intercoolers to minimize the compression work and operate at constant throughput, delivering the syngas at constant pressure and temperature to the synthesis reactor. The synthesis loop operates adiabatically at constant pressure with a slight pressure drop across the reactor beds [12].

#### 2.1 Air separation unit cost analysis

Air separation units are rated in terms of normal cubic meters per hour which is the volume of the gas at standard temperature and pressure. An ammonia production facility with a capacity of 300 ton/day is considered in the analysis. Using the ideal gas law at STP to convert a mass of 246.7 tons of nitrogen to units of meters cubed gives a volume of 214,500 m<sup>3</sup>/day or about 8,940 m<sup>3</sup>/h. The molecular mass of water is approximately 16 g/mol and 1 g of water equals one mL so the total volume of water required can be calculated. A 300 ton per day ammonia plant will require about 476 tons of distilled water/day. The flow rates of nitrogen, ammonia, hydrogen and water are summarized in Table 13, respectively.

Product	Daily Amount (ton/day)	Flow Rate (kg/h)
Nitrogen	246.7	10,280
Hydrogen	53.3	2,220
Water	476	19,830
Ammonia	300	12,500

Table 13. The mass flow rates of feed gases, water and ammonia product in a 300 ton/day ammonia production facility

Note that the power required for air separation is almost solely from the compression train used at the inlet and depends on the design of the plant. The assumptions for the air separation plant are: the intake temperature is 298 K, there are 3 stages of compression to raise the pressure to 8 bar and the recovery ratio of the air separation plant is 70% by volume. The total volumetric flow rate of air into the compression train is the total nitrogen production capacity divided by the recovery ratio:

$$\dot{V}_{air} = \frac{V_{N_2}}{\eta_{ASU}}$$

.

A 300 ton/day ammonia plant will require 247 ton/day or 8940 Nm<sup>3</sup>/h of nitrogen. Thus, the air intake into the first compressor of the ASU will be 352.8 ton/day which corresponds to 4.08

kg/s. The fluid power required is 792 kW. If an adiabatic compressor efficiency of 75% is assumed together with a driver efficiency of 95%, the total power required will be 1.112 MW. Specifications and costs of heat exchangers used in ASU plant are shown in Table 14 with 2010 US \$ prices.

Туре	Area (m <sup>2</sup> )	Pressure (bar)	Uninstalled Cost (\$)	Installed Cost (\$)	
Floating head	121.32	2	38,340	83,200	
Floating head	127.56	4	39,280	85,240	
Floating head	188.19	8	48,550	105,350	
Plate fin	2855.69	8	514,910	1,428,880	
Total	3292.76		641,080	1,702,670	

Table 14. Specifications and cost of heat exchangers used in ASU plant based on 2010 US\$

Source: Data from Ref. [13]

The main heat exchanger in a cryogenic air separation facility is the cold box which is a large multi stream brazed aluminum heat exchanger that cools incoming warm air against the cooler waste and product streams. The intercoolers are standard, water cooled, liquid-gas heat exchangers. The process air stream is assumed to be cooled to the inlet temperature at each step, which is a function of the pressure increase across the compressor.

Table 15. Specifications and cost	of compressors ar	nd drivers used in	ASU plant based	on 2010
	TICA			

Туре	Number	Compressor power (MW)	Driver Power (MW)	Uninstalled Cost (\$)	Installed Cost (\$)
Centrifugal & Driver	1	379	505.3	285,770	654,560
Centrifugal & Driver	1	362.3	483.1	277,430	633,730
Centrifugal & Driver	1	413.5	551.3	302,540	696,580
Total	3				1,984,870

Source: Data from Ref. [13]

	U	20		
Туре	Volume (m <sup>3</sup> )	Pressure (bar)	Installed Cost (\$)	Installed Cost (\$)
High pressure distillation column	134.9	6	120,800	1,658,670
High pressure distillation column	175.3	1.8	153,700	1,260,050
Argon distillation column	22.5	1.3	27,710	227,170
Total			302,210	3,145,890
~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~				

Table 16. Specifications and cost of towers used in 250 ton N<sub>2</sub>/day ASU plant based on 2010

Source: Data from Ref. [13]

It is assumed that standard carbon steel, centrifugal compressors are used since air is relatively inert and non-corrosive. The cost of these machines is related to the fluid power required in the application. The cost of compressors, towers and turbines used in ASU plant are given in Tables 15, 16 and 17, respectively. The drivers are assumed to be totally enclosed all electric motors made of carbon steel. They are subjected only to ambient pressures and temperatures, and do not come into contact with any corrosive substances.

Table 17. Specifications and cost of turbine used in 250 ton N<sub>2</sub>/day ASU plant based on 2010 US\$

Туре	Material	Power (kW)	Uninstalled Cost (\$)	Installed Cost (\$)
Radial gas	Carbon steel	25	14,590	89,000
Source: Data	from Ref. [13]			

In total, the capital cost of 250 ton N<sub>2</sub>/day ASU plant corresponds to 6,922,430 \$.

#### 3. Feasibility analysis of Haber-Bosch ammonia synthesis loop

The major process equipment in an ammonia synloop consist of compressors, heat exchangers, pumps and the reactor. The compressor sizing is straightforward and is primarily driven by the flow rates and pressure ratios. The cost of the process equipment depends on three major factors: the size, the material of construction and the operating pressure. Also, pressure affects the cost of process equipment because higher pressures often require more material and heavier frames. While there are a many of ammonia synthesis loop configurations some basic assumptions enable an economic analysis which is valid for any synthesis loop. The assumptions are as follows: A centrifugal compressor train takes the feed gas from 1 bar to operating pressure. A recycle compressor is used to compensate for the pressure drops in the loop. The operating pressures and temperatures are valid for any size ammonia plant. The calculations for a 300 ton/day ammonia production facility are based on Ref. [13]. Compression work for hydrogen can be done within the electrolyzer instead of by compressors. This approach simplifies the overall process and saves capital cost expenses for the compression machinery including drivers and compressors. The

compression work must be the same for both processes, and the derivation that appeared in Larminie and Dicks [14] is given below:

$$\Delta W_{compressor} = PV \ln\left(\frac{P_2}{P_1}\right) = nRT \ln\left(\frac{P_2}{P_1}\right)$$
$$\Delta U = \frac{RT}{zF} \ln\left(\frac{P_2}{P_1}\right)$$
$$\Delta W_{compressor} = \Delta U \cdot Q$$

$$\Delta W_{compressor} = \Delta U \cdot zF \cdot n$$
  
$$\Delta W_{compressor} = \frac{RT}{zF} \ln \left(\frac{P_2}{P_1}\right) \cdot zF \cdot n = nRT \ln \left(\frac{P_2}{P_1}\right)$$

Here, for the feed stream, it is assumed that the hydrogen is available at STP from the electrolyzer bank, nitrogen is at standard temperature and 8 bar from the ASU. The fluid compression power required is given by following equation:

$$\dot{W}_{fluid} = T_{in}N\frac{n}{n-1}R\dot{m}\left[\left(\frac{P_2}{P_1}\right)^{\frac{1}{N}}\right]^{\frac{n-1}{n}} - 1\right]$$

where  $T_{in}$  is the temperature of the feed gases incoming the compressor in Kelvin; N is the number of stages in the compression train; n is the polytrophic exponent; R is the specific gas constant in kJ/kgK;  $\dot{m}$  is the mass flow rate in kg/s;  $P_2$  is the final pressure in bar;  $P_1$  is the initial pressure in bar. The term gives the compression ratio across each compressor. If isentropic compression is assumed, the temperature is raised across each compressor. Intercooling is utilized between the stages to minimize the compressor work. Thus, each intercooler must remove the heat imparted on the feed gas by the compressors. It is assumed that the intercoolers cool the gas down to the inlet temperature of the compressor. In this case, each compressor has the same conditions and uses the same amount of power. The hydrogen and nitrogen are available at the compressor inlet at two different pressures. The total compression power is the sum of the compression for each component. The conditions for each component of the feed are given in Table 18.

Table 18. Assumptions of operating conditions for the capital cost analysis in the ammonia

synthesis loop						
Parameter	Value					
T <sub>in</sub> (°C)	25					
Pout (bar)	150					
Pin Nitrogen (bar)	8					
Pin Hydrogen (bar)	1					
R <sub>H2</sub> (kJ/kgK)	4.124					
R <sub>N2</sub> (kJ/kgK)	0.2968					

The compression power required is linear with the flow rate of feed gas, given any synloop operating pressure. This further implies that the size of the compressors and the drivers for the compressors is also linear with flow rate. Following figure shows the fluid compression power required for various ammonia plant capacities.

The power required to drive the compressor is the fluid power divided by the isentropic efficiency of the compressor, as shown in the following equation:

$$\dot{W}_{shaft} = \frac{\dot{W}_{fluid}}{\eta_s}$$

The isentropic efficiency is taken to be 75%. Thus, the actual power needed at the shaft is about 25% higher than required by the fluid.

The recycle compressor is tasked with compressing more mass than the feed stream but with a smaller pressure ratio. The conversion efficiency refers to the conversion rate of ammonia in the synthesis reactor and is generally about 15%. Therefore, the synloop has roughly 6 times the flow rate of the feed gas and contains ammonia as well as the hydrogen and nitrogen from the feed. The pressure drop around the synthesis loop varies with the configuration, and operating parameters of the entire plant. However, a total pressure drop of about 6% can be assumed as a baseline to determine the total compression power of the recycle compressor [15].



Fig. 15. The required compression power for hydrogen and nitrogen gases in the ammonia synthesis loop (adapted from Ref. [13])

Each compressor is driven by its own drivers. The power requirements for the compression are determined by dividing the shaft power of the compressor by the efficiency of the electric motor. The electric motor efficiency is generally more than 90% and rises with the rated operating power and the turndown ratio. Because the ammonia synthesis occurs at steady state and the compression power required for small plants is in the MW range, an efficiency of 95% is assumed for this analysis. The isentropic efficiency is taken to be 75%, and the efficiency of the driver is

taken to be 95%. The power requirements of the compressors in synloop are given in Table 19. The driver power can be written as follows:

$$\dot{W}_{driver} = \frac{\dot{W}_{fluid}}{\eta_s \cdot \eta_{driver}}$$

Ammonia plant capacity (ton/day)	Total fluid power (MW)	Shaft power (MW)	Driver power (MW)
100	1.88	2.50	2.64
200	3.76	5.01	5.27
300	5.62	7.51	7.91
400	7.51	10.02	10.54
500	9.39	12.52	13.18

Table 19. The power requirements for the compressors in the synloop based on various ammonia production capacities

Source: Data from Ref. [13]

For any ammonia plant size, the flows of reactants and products throughout the plant can be calculated. The flow rates through the system are determined from the stoichiometry of ammonia. The chemical formula for ammonia is NH<sub>3</sub>, its molecular mass is 17.03 g/mol of which nitrogen is approximately 14 g/mol. NH<sub>3</sub> consists of 82.4% nitrogen and 17.6% hydrogen by weight. Thus, nitrogen and hydrogen must be mixed in the proper proportions and reacted together to form ammonia. Therefore, for 300 ton/day ammonia plant will require about 246.7 tons of nitrogen and 53.3 tons of hydrogen per day. Specifications and cost of heat exchangers and compressors used in the synloop are given in Tables 20 and 21, respectively.

Area (m <sup>2</sup> )	Capacity (MW)	Installed Cost (\$)
1690	4.60	3,016,600
28.5	3.31	219,610
332.2	5.72	610,520
197.5	10.67	427,770
176.8	4.35	400,450
2425	28.64	4,674,950
	Area (m <sup>2</sup> ) 1690 28.5 332.2 197.5 176.8 2425	Area (m²)       Capacity (MW)         1690       4.60         28.5       3.31         332.2       5.72         197.5       10.67         176.8       4.35         2425       28.64

Table 20. Specifications and cost of heat exchangers used in the synloop based on 2010US\$

Source: Data from Ref. [13]

The heat exchangers are required to integrate the heat throughout the synthesis loop. There are assumed to be four major heat exchangers in the loop that are tasked with heating up the feed gases that enter the reactor and cooling down the product streams as they leave the reactor. There

are also intercoolers that cool the gases between compression stages to minimize the compressor work.

		US\$		
Туре	Number	Fluid Power (MW)	Shaft Power (MW)	Installed Cost (\$)
Centrifugal & Driver	5	1.02	1.54	2,499,210
Centrifugal & Driver	1	0.52	0.78	1,630,920

Table 21. Specifications and cost of compressors and drivers used in the synloop based on 2010

Source: Data from Ref. [13]

Total

Table 22. Specifications and cost of reactors used in the synloop based on 2010 US\$

5.62

8.48

14,126,970

Туре	Volume (m <sup>3</sup> )	Pressure (bar)	Installed Cost (\$)	
Packed bed	7.54	150	1,686,900	
Flush drum	6.1	150	1,477,900	
Total			3,164,800	
Source: Data from Def [12]				

Source: Data from Ref. [13]

6

The installed costs of Haber-Bosch reactor and reciprocating pumps are given in Table 22 and 23, respectively.

Table 23. Specifications and	cost of pump	used in the synloop	based on 2010 US\$
		2 1	

Туре	Material	Power (kW)	Installed Cost (\$)	
Reciprocating	Carbon steel	112	581,840	
Source: Data from Ref. [13]				

In total, ammonia synthesis loop capital cost yields 22,548,560 US\$.

#### 4. Feasibility analysis of electrolyzers in hydrogen production process

The power requirements for electrolysis of water can be calculated using the manufacturer specifications for the specific power requirements. For example the specific power for Norsk Hydro Atmospheric Type 5040 electrolyzers is listed as  $4.8 \text{ kWh/Nm}^3$  of hydrogen, of which  $4.3 \text{ kWh/Nm}^3$  is for electrolysis and the remaining  $0.5 \text{ kWh/Nm}^3$  is for the balance of plant. The calculation for the power requirements for a 26,800 Nm<sup>3</sup>/h of hydrogen consuming ammonia plant is:

$$P_{elec} = (4.8) \frac{\text{kWh}}{\text{Nm3}} (26,800) \frac{\text{Nm3}}{\text{h}} = 129 \text{ MW}$$

This is the direct current (DC) power requirement for electrolysis. The alternating current (AC) power requirements are calculated by dividing the DC power requirement by a rectifier efficiency of 95% [16] to obtain 135.4 MW.



Fig. 16. The capital cost distribution of all electric 300 ton/day ammonia production plant (data from Ref. [13])



Fig. 17. Capital cost curve for an all-electric ammonia plant (adapted from Ref. [13])

On the other hand, for the central electrolysis which was given in the previous section, the average energy consumption rate is 46 kWh/kg which corresponds to 4.14 kWh/Nm<sup>3</sup>. In this case, the required power is:



 $P_{elec} = (4.14) \frac{\text{kWh}}{\text{Nm3}} (26,800) \frac{\text{Nm3}}{\text{h}} = 111 \text{ MW}$ 

Fig. 18. Power requirements of all-electric ammonia plants for various capacities (adapted from Ref. [13])

When electrolyzer scaling is used, the electrolyzer stacks share common industrial equipment to reduce costs. The best case scenario is has a cost curve with a scaling factor of 0.5, and overall capital costs are drastically reduced. The power requirements are almost entirely for the electrolysis of water. For a 300 ton/day ammonia plant, the power requirements are calculated to be 145 MW total with 135 MW being required for the electrolysis which corresponds to 93% as shown in Fig. 18. The synthesis loop requires about 8 MW of power, or about 5.5% of the total power requirements. The power required for a 300 ton/day ammonia plant is about 145 MW. Thus, the plant will consume 1,148,400,000 kWh of energy annually. The overall capital cost distribution in a 300 ton/day ammonia production facility can be seen in Figs. 16 and 17 (with electrolyzer scaling).

#### II. CASE STUDIES

In this section, various case studies ranging from high pressure electrolysis process to thermal methane plasma disassociation are comparatively studied. Possible improvements in Haber-Bosch process are investigated by eliminating the main feed gas compressor and utilizing the excess heat in the reactor. The feasibility study of the selected options have been conducted.

## **Case 1: Ammonia production via low cost hydropower electricity + high pressure electrolysis** + **cryogenic air separation + Haber-Bosch plant without compressor**

The average cost of ammonia production from the electrolysis based systems are approximately 20-25% of hydrogen production cost as previously given in Ref. [17] for various ammonia production methods. 17.8% of ammonia is hydrogen in weight, and about 3% of ammonia production cost comes from air separation based nitrogen production. In the proposed system, the lower limit has been taken to calculate the cost of ammonia production from high pressure electrolysis based systems. Therefore, ammonia production costs are calculated as the 20% of hydrogen production cost. The schematic diagram of high pressure electrolysis based ammonia production system is given in Figs. 19 and 20. In this case, hydrogen compressor is eliminated by using pressurized water and high pressure electrolysis system. However, the nitrogen is used as gaseous form and still need to be compressed by the compressor. The amount of work decreases substantially because nitrogen constitutes about 82% of the feed gases. The required electricity is supplied via low cost hydroelectric plant to the electrolyzer, cryogenic air separation unit, external nitrogen compressor, pump and recycling compressor inside the Haber Bosch process.



Fig. 19. Schematic diagram of high pressure electrolysis based ammonia production system



Fig. 20. A diagram of energy and material flows of high pressure electrolysis based ammonia production system

Using the data from the previous chapter given in high pressure electrolysis hydrogen production prices, the costs of ammonia production via high pressure electrolysis based electrolysis at two different electricity prices are illustrated in Fig. 21.



Fig. 21. Cost comparison of ammonia production from high pressure PEM electrolysis and Haber-Bosch plant based on various electricity price and current electrolyzer densities at 345 bar (data from Ref. [2])

## Case 2: Ammonia production via low cost hydropower electricity + high pressure electrolysis + cryogenic air separation with liquid nitrogen pumping + Haber-Bosch plant without main compressor

In this case, opportunities of utilizing the excess heat of Haber Bosch process are investigated as illustrated in Fig. 22 and 23. The negative value of enthalpy in the ammonia synthesis process indicates that the reaction is exothermic, releasing approximately 2.7 GJ/ton NH<sub>3</sub> heat in ammonia production. This is equivalent to about 8% of the energy input for the entire process. It means that heat dissipation is about  $\dot{Q}_{HB,Specific} = 2700 \text{ kJ/kg}$  ammonia. For the ammonia production facility with a capacity of 300 ton/day, the amount of required nitrogen mass flow rate is 246.7 ton/day which corresponds to about 2.90 kg/s.



Fig. 22. Schematic diagram of high pressure electrolysis and liquid nitrogen pumping based ammonia production system

In this case, hydrogen is produced via high pressure electrolysis and sent to Haber-Bosch reactor. Nitrogen is produced by cryogenic air separation as liquid end product. The liquefaction of nitrogen process will require more energy compared to gaseous end product. The liquid nitrogen is pumped to reaction pressure about 200 bar by cryogenic pump.



Fig. 23. A diagram of energy and material flows of high pressure electrolysis and liquid nitrogen pumping based ammonia production system

The excess heat in Haber-Bosch reactor is utilized for the vaporization of high pressure liquid nitrogen to obtain high pressure gaseous nitrogen for ammonia synthesis reaction. The required electricity is supplied via low cost hydroelectric power plant to the electrolyzer, cryogenic air separation unit, pumps and recycling compressor inside the Haber Bosch process.

An air separation facility with a capacity of about 250 ton/day is considered. The outlet pressure of air separation unit is generally at 8 bar. The liquid nitrogen at 8 bar is pressurized using cryogenic pumps up to 200 bar.

#### $\dot{m}_{N_2} \cdot h_{liquid\ nitrogen\ 1} + \dot{W}_{Pump} = \dot{m}_{N_2} \cdot h_{liquid\ nitrogen\ 2}$

The required pump power is calculated as 52.36 kW. The liquid nitrogen enters to vaporizer which utilizes the excess heat in Haber-Bosch process. The outlet temperature of vaporized unit is set to  $25^{\circ}$ C.

 $\dot{m}_{ammonia} = 300 \cdot \frac{1000}{24 \cdot 3600} \text{ kg/s}$  $\dot{m}_{hydrogen} = 53.3 \cdot \frac{1000}{24 \cdot 3600} \text{ kg/s}$ 

.

 $\dot{Q}_{Haber Bosch} = \dot{m}_{ammonia} \cdot \dot{Q}_{HB,Specific}$ 

When 300 ton/day ammonia is produced, the Haber-Bosch reactor releases 9375 kW heat. The hydrogen and nitrogen gas mixture is sent to reactor. The reaction temperature for Haber-Bosch process is about 450°C. The temperature of hydrogen is assumed as 100°C after high pressure electrolysis. The required heat of vaporization for nitrogen at T2 = -180°C is calculated as 506.1 kW.

$$\dot{Q}_{Haber Bosch} = \Delta h_{vaporization, liquid nitrogen} \cdot \dot{m}_{N_2}$$

Besides, the mixture gasses hydrogen and nitrogen require 4589 kW heat in order to reach the reaction temperature.

$$Q_{Hydrogen} = \dot{m}_{hydrogen} \cdot (h_{hydrogen 2} - h_{hydrogen 1})$$
$$\dot{Q}_{Nitrogen} = \dot{m}_{nitrogen} \cdot (h_{nitrogen 2} - h_{nitrogen 1})$$

where initial temperature of hydrogen is 100°C and initial temperature of nitrogen is 25°C, and final temperature is 450°C.

$$\dot{Q}_{Reaction Temperature} = \dot{Q}_{Hydrogen} + \dot{Q}_{Nitrogen}$$
  
 $\dot{Q}_{Excess Heat} = \dot{Q}_{Haber Bosch} - \dot{Q}_{Reaction Temperature}$ 

Therefore, 4786 kW excess heat is available which can be utilized in vaporization of liquid nitrogen. Finally, the amount of excess heat from Haber-Bosch reactor is satisfactorily enough for the vaporization of liquid nitrogen. On the other hand, if gaseous nitrogen is pressurized to the reaction temperature instead of liquid pumping, the required compressor power to have compressed nitrogen from 8 bar to 200 bar is calculated to be 1057 kW. In total, liquid nitrogen pumping and vaporization require about 559 kW power. This indicates that there is about 52% reduction in energy requirement by using liquid nitrogen pumping and vaporization obtained by the excess reactor heat. As it can been seen in previous tables, the cost of 5 centrifugal compressors in the 300 ton/day ammonia synthesis synloop represent 50% of the overall installed cost of synthesis loop. When these compressors are eliminated, nearly 11 million \$ capital cost reduction will be achieved.

The required power for 300 ton / day ammonia plant was calculated as 145 MW. Approximately 7.7 MW of this power is used for synloop compressors. Therefore, the required power will decrease 5.3% for the overall plant.

# Case 3: Pressurization of LNG to 200 atm and vaporization of LNG using waste heat from Haber-Bosch reactor + Plasma dissociation of methane for hydrogen production via low cost hydropower electricity + Cryogenic air separation with liquid nitrogen pumping + Haber-Bosch plant without main compressor

In this case, methane is utilized as a source of hydrogen which is required for ammonia production as shown in Fig. 24. Rather than steam methane reforming, thermal plasma cracking of ammonia is an important option for clean ammonia production.

Methane (CH4) is dissociated to carbon (C) black and hydrogen (H2) according to:

$$CH_4 \rightarrow C + 2 H_2 \Delta H = 74.9 \frac{kJ}{mol} at 25^{\circ}C.$$

Here, methane is a favored option for H<sub>2</sub> production from a hydrocarbon because of its high H to C ratio, availability and low cost. Furthermore, the C produced can be sold as a co-product into the carbon black market which could be utilized in inks, paints, tires, batteries, etc. or sequestered, stored, and used as a clean fuel for electricity production. The sequestering or storing of solid C requires much less development than sequestering gaseous CO<sub>2</sub> [18].





As seen in Fig. 24, liquid natural gas and liquefied natural gas is pressurized using cryogenic pumps. The available excess heat from Haber-Bosch reactor is utilized for vaporization of both liquid nitrogen and LNG. The high pressure LNG is sent to thermal plasma disassociation process which divides methane into hydrogen and carbon. Carbon black is stored for further utilization is various industries. The obtained hydrogen gas is transferred to Haber-Bosch process together with high pressure nitrogen gas.

It is a plasma-arc process that decarbonizes natural gas in a compact reactor that is in-line with the fuel delivery system. The carbon has applications in metallurgy, tires and manufactured rubber goods. Carbon black is a form of carbon that is usually created by the incomplete combustion of heavy petroleum products. It is primarily used as a rubber reinforcing agent in the production of automobile tires, belts and hoses, as well as a pigment in plastics and dyes [19].

The commercial microwave disassociation of methane requires the equivalent of between 3-4 kWh/m<sup>3</sup> of pure H<sub>2</sub> [19]. The voltage required to produce the plasma depends on many factors such as the plasma distance, the type of media used, the operating pressure, and the operating temperature. Typically the system plasma voltages change from 1 kV – 20 kV. The actual plasma temperature is between 1500°C-2500°C. The exiting gas temperature may reach 300°C and the reactor surface temperature is generally less than 200°C. The theoretical efficiency limit for the plasma technology is less than 1 kWh/m<sup>3</sup> of pure H<sub>2</sub> [19]. The estimated cost would be equivalent to \$0.05 per 28.2 m<sup>3</sup> of natural gas or about a 1% premium paid on the price of gas [19]. The carbon can be sold to foundry industry with an average price of 900 US\$/ton.

Thermal plasma disassociation of methane would bring some problems under high pressure since there is not much study about even moderate pressure systems. In the analysis, it is assumed that the pressure will not affect the conversion process.

The calculations are carried out for a 300 ton/day ammonia production plant which utilizes thermal plasma disassociation of methane for hydrogen production based on the data in Ref. [20]. The following assumptions are made:

- The thermal efficiency of DC-RF microwave unit is assumed to be 60% [20].
- The methane is totally converted to hydrogen and carbon black.
- Hydrogen and methane is assumed to be at ambient temperature at 25°C and pressure P=100 kPa.
- Carbon yield is 0.49 kg/m<sup>3</sup> natural gas at STP.
- The price of carbon black is assumed to be 1 US\$/kg in economic calculations.

The outlet pressure of air separation unit is generally at 8 bar. The liquid nitrogen at 8 bar is pressurized using cryogenic pumps up to 200 bar.

#### $\dot{m}_{N_2} \cdot h_{liquid\ nitrogen\ 1} + \dot{W}_{Pump} = \dot{m}_{N_2} \cdot h_{liquid\ nitrogen\ 2}$

The required pump power is calculated as 52.36 kW. The liquid nitrogen enters to vaporizer which utilizes the excess heat in Haber-Bosch process. The outlet temperature of vaporized unit is set to 25°C. When 300 ton/day ammonia is produced, the Haber-Bosch reactor releases 9375 kW heat. The hydrogen and nitrogen gas mixture is sent to reactor. The reaction temperature for Haber-Bosch process is about 450°C. The temperature of hydrogen is assumed as 100°C after high pressure electrolysis. The required heat of vaporization for nitrogen at T = -180°C calculated as 506.1 kW.

 $\Delta h_{vaporization,LNG} = Entalpy_{vaporization}(Methane, T = T_NG2)$  $\dot{Q}_{Vaporization,LNG} = \Delta h_{vaporization,LNG} \times \dot{m}_{N_2}$
The required energy for vaporization of LNG is found to be  $\dot{Q}_{Vaporization,LNG} = 1257$  kW for LNG at  $T_{NG2} = -161^{\circ}C$ . The mass flow rate of natural gas and carbon can be found as per following formula:

$$\dot{m}_{carbon} = \dot{V}_{natural\ gas} \times 0.49 \text{ kg/s}$$

$$\dot{m}_{natural\ gas} = \frac{v_{natural\ gas}}{v_{natural\ gas}}$$

 $\dot{W}_{pump,LNG} = v_{natural gas} (P_2 - P_1)$ 

The required pump work for LNG from 1 bar to 200 bar kPa is found to be  $\dot{W}_{pump,LNG} = 47.09$  kW.

 $\dot{m}_{NG} \cdot h_{NG1} + \dot{W}_{Compressor} = \dot{m}_{NG} \cdot h_{NG2}$ 

If a compressor is used from ambient temperature and pressure at 25°C and 1 bar to 200 bar for natural gas instead of LNG pumping, the required power would be  $\dot{W}_{compressor,ambient} = 518.8 \text{ kW}$ . If the compressor works under same conditions with pump which is from -162°C, the outlet temperature becomes 147°C and the required power yields  $\dot{W}_{compressor} = 1503 \text{ kW}$ .

<b>Product/Feed</b>	Mass Flow Rate (kg/s)
Carbon	1.863
Hydrogen	0.6169
Natural gas	2.465
Nitrogen	2.894
Ammonia	3.472

Table 24. The mass flow rates of the streams in the process

For the 300 ton/day ammonia plant, the mass flow rates of the streams in the thermal plasma disassociation process are given in Table 24. As previously calculated, 4786 kW excess heat was available which can be utilized in vaporization of both liquid nitrogen and LNG. The total required heat for vaporization processes is 1,257 kW+ 506.1 kW=1,763.1 kW. Finally, the amount of excess heat from Haber-Bosch reactor is satisfactorily enough for the vaporization of both liquid nitrogen and LNG.

Thermal plasma disassociation balance equation can be written as follows:

 $\dot{m}_{NG} \cdot h_{NG} + \dot{W}_{in,thermal \ plasma \ disassociation} = \dot{m}_{H_2} \cdot h_{H_2} + \dot{m}_{carbon} \cdot h_{carbon}$ 

The required power input to the thermal plasma disassociation system is calculated to be  $\dot{W}_{in,thermal \, plasma \, disassociation} = 115,853 \, \text{kW}.$ 

The total required power for a high pressure electrolysis based ammonia production plant with a capacity of 300 ton/day ammonia was calculated to be about 145 MW. For this case, it is about 116 MW which is 20% less.

The cost of hydrogen production via thermal plasma disassociation is given in Table 25 based on the previously mentioned assumptions. The hydrogen purity from methane disassociation is 98%. PSA unit included in CarbonSaver plant cost to achieve 99.9% hydrogen purity. In the cost analysis, it is assumed that the plant has a capacity of 1,500 kg/day, plant life is 20 years and capacity factor is 70%.

Based on the assumption that ammonia production cost will be about 20% of hydrogen production cost, the price is calculated as 1.01 \$/kg ammonia. However, when the carbon black sales are taken into account, it decreases down to 0.412 \$/kg.

Category	Cost (US\$/kg H <sub>2</sub> )
Capital	0.46
O&M	1.40
Feedstock	3.19
Total	5.05
Carbon Black Sales	-2.99
Net Cost	2.06
Source: Data from Ref	. [21]

Table 25. Cost of hydrogen production using thermal plasma disassociation of methane

#### Case 4: Using pumped hydro or producing ammonia from the excess power in Niagara

Pumped hydroelectric storage plants store energy in the form of water in an upper reservoir, pumped from another reservoir at a lower elevation. During periods of high electricity demand, power is produced by releasing the stored water through turbines with the same method of hydropower plants. During low demand periods which are generally nights or weekends, the upper reservoir is charged via low cost electricity from the grid to pump the water back to upper reservoir. The efficiency values of pumped storage systems are high where the average efficiency values of system components in pumped storage plants are shown in Table 26.

	Efficiency of generating cycle in average (%)	Efficiency of pump cycle in average (%)
Water conductors	98.3	98.3
Pump	83	91
Motor	98.1	98
Transformer	99.3	99.3
Overall	78.5	87.1

Table 26. Average efficiency values of system components in pumped storage plants

Source: Data from Ref. [22]

The Ontario Power Generation operates a pumped storage plant near Niagara. It was constructed when Ontario projected excess nuclear production. Although it wastes one unit of electricity for each unit finally delivered, the storage system reserves some of the nightly water flow over Niagara for daytime use. This time-shifting optimizes power production by the main generators, while maintaining the scenic daytime water flow over Niagara Falls as required under international agreement.

	φ/ 1 <b>v1 vv 11</b>
Project	3 Year Average O&M Cost in 2009 \$/MWh
Bad Creek	3.41
Bath Country	2.43
Cabin Creek	15.42
Fairfield	4.11
Helms	19.44
Jocasse	5.07
Ludington	5.55
Rocky Mountain	6.64
Yards Creek	5.28
	6 [22]

Table 27. Three year average O&M costs of various hydro pumped storage projects in 2009 \$/MWb

Source: Data from Ref. [22]

In Table 27, the O&M cost data do not include energy for pumping purposes. The average O&M cost is about \$9.95/MWh as shown in Table 27 and Table 28. It is expected that specific construction and equipment procurement cost for a 1000 MW pumped storage project is a little under 2000 \$/kW. The specific cost is close to 4000 \$/kW for small projects on the order of 30 MW. The current capital cost of new pumped hydro facilities is estimated to range between USD 2 000-4 000/kW as shown in Table 28.

Capacity (MW)	Specific Installation Cost (\$/kW)	Estimated Annual O&M Cost (million \$ in 2009)
50	3000	1.5
100	2940	2.9
250	2750	6.9
500	2500	12.5
750	2250	16.9
1000	2000	20

Table 28. Specific installation and estimated annual O&M costs for pumped storage hydro plants

Source: Data from Ref. [22]

The Lewiston Pump-Generating Plant located in Niagara has an installed power of 240 MW. The water is pumped at night since the demand for electricity is much lower than during the day. In addition to the lower demand for electricity at night, less water can be diverted from the river during the day because of the desire to preserve the appearance of the falls. During the following day, when electrical demand is high, water is released from the upper reservoir through the pump-generators in the Lewiston Dam. In Ontario, there is only one pumped hydro storage facility in operation, the Sir Adam Beck Pumped Storage Facility in Niagara Falls. During off-peak periods (night time), Ontario Power Generation diverts water from the Niagara River, filling its 300 hectare reservoir. During peak periods, this water is released, creating up to 174 MW of

hydro power. The capacity factor of the pumped storage power plants is about 6 hours/24hours=25%.

For a pumped storage hydro plant with a capacity of 142 MW, a reversible Francis pump turbine system is necessary to pump back the water to the upper reservoir. Each pump/turbine will have a flow rate of  $38.857 \text{ m}^3$ /s. The system is planned to charge for 7 hours; with 81%

$$\dot{W}_{input,pump} = \frac{\rho \cdot g \cdot H \cdot Q}{\eta}$$

where  $\rho$  stands for the density of the fluid to be pumped, g is for acceleration due to gravity and H, Q stands for both gross head in meters and volumetric flow rate, respectively. Here  $\eta$  is the efficiency of pump considering all components water conductors, pump, motor, transformers. The pump power needed is calculated to be about 142 MW. The cost of storage unit is directly dependent on the stored energy and inversely proportional to the efficiency of the system.

As an example, the tariff of electricity is taken as follows: 0.4736 %/kWh for peak hour and 0.3664 %/kWh for off-peak hour. The power for the pump will be used from off-peak hours starting from midnight.

#### Peak hour energy discharge $cost = Discharging hours \times Peak hour cost$

There are 5.67 hours of discharge and it works for the whole year.

Peak hour energy discharge cost = 
$$5.7 \frac{hours}{day} \times \frac{365 \, day}{year} \times \frac{0.4736 \, \$}{kWh} = \frac{980.1 \, \$}{kW \, year}$$

Energy charging cost (of f – peak hour energy) = Charging hours × of f – peak hour cost

There are seven hours of charging.

Energy charging cost = 
$$7 \frac{hours}{day} \times 365 \frac{day}{year} \times 0.3664 \frac{\$}{kWh} = 936.2 \frac{\$}{kWyear}$$

The cost reduction available is 43.9 \$/kW year.

For a 145 MW pumped storage power plant, the overall yearly benefit would be calculated as  $43.986 \frac{\$}{kW} \times 145000 \, kW = 6,377,970 \,\$.$ 

Here, the specific installation cost of pumped storage plants is about 2,750 \$/kW which yields 398.75 million \$ capital cost for installation. Annual estimated O&M cost of 150 MW pumped storage power plant is about 4.2 million \$.

As it was analyzed in the previous cases, ammonia production facility requiring about 145 MW installed power would produce 300 ton/day ammonia. This will correspond to 109,500 ton/year. The lowest ammonia production cost which was calculated in high pressure electrolysis based system yields 760 US\$/ton. If the selling price of ammonia is assumed to be about 800 US\$/ton in the current market, there is 40 US\$/ton profit from ammonia trade. Yearly, there is about 4,380,000 US\$ profit. The O&M cost of ammonia plant is calculated by multiplying the number of operating hours which is about 8000 hours/year by the electricity price by the operating power. Thus, the operating cost in year 1 is approximately \$931,000 which is much lower than pumped storage hydro plant.

#### **Case 5: Wind based ammonia production cost analysis**

The offshore wind energy is an alternative source for power generation which can be utilized in high pressure electrolyzers. The baseline offshore wind powered ammonia plant was simulated using the wind data from the Gulf of Maine. The simulation was done for a three year period using wind and grid from 2005-2007 [13]. The results are averaged over the three year period to get one representative year of system outputs as shown in Table 29. The 300 MW plant, which includes the NH<sub>3</sub> facility and the offshore wind farm, had a total capital cost of \$1.39 billion 2010 dollars [13].

The LCOA (levelized cost of ammonia) calculation requires several economic assumptions be made about the loan and the interest rates associated with the investment. The levelized cost calculation has several parts. First, the down payment on the investment is assumed to be in year 0 and is already in present value. For simplicity, the down payment is assumed to be 10% of the capital expenditure, or \$139 million for the base case. The second term in the equation calculates the present value of the payments on the loan. Four parameters are required: the total value of the in present dollars, the interest rate on the loan, the inflation rate over the lifetime of the system, and the lifetime of the loan. The total amount of the loan is simply the total capital expenditure minus the down payment, or \$1.251 billion dollars. The interest rate is assumed to be 4% with the inflation rate at 3%; the discount rate is assumed to be 7%. The lifetime of the project is assumed to be 20 years, which is typical for wind farms and chemical processing plants. The loan life is 15 years. The third term in the LCOA equation calculates the present value the operations and maintenance costs for the lifetime of the system - 20 years in this case. Recently, the operations and maintenance cost for onshore wind farms was found to be \$10/MWh, corresponding to about 2.4% of the capital expenditure [23]. Because the wind farms are offshore rather than onshore, a higher value of 3% of the capital expenditure is assumed for this analysis.

Parameter	Value
Capacity factor (%)	40.92
Average wind speed (m/s)	9.62
Average power (MW)	122.75
Annual electricity sold (MWh)	296,300
Annual electricity purchased (MWh)	492,000
Ammonia sold (ton)	109,500
Overall ammonia conversion efficiency (%)	50
Total cost (billion \$)	1.39

|--|

Source: Data from Ref. [13]

The wind farm achieved a capacity factor of over 40% and required more than 534 GWh of electricity from the grid to sustain the ammonia production process. At the same time, a substantial amount of energy could be sold back to the grid, totaling more than 268 GWh. The capital cost distribution of offshore wind based ammonia production plant is shown in Fig. 25.

The cost of manufacture for the ammonia facility is of principal importance: a large fraction of the overall costs will come from purchasing electricity, assumed to be the utility cost. The cost of manufacture is the sum of waste disposal, labor costs, utilities, general expenses, raw materials, taxes, maintenance costs as well as other minor costs. The waste disposal is assumed to be negligible because the waste is oxygen or brine both of which can be discharged safely into the environment with little or no processing. The following economic assumptions are made: Discount rate is 7%, inflation rate is 3%, interest rate is 4%, loan life is 15 Years, project life is 20 Years, O & M fraction for wind is 3% of capital expenditure and down payment is 10% of total capital cost [13].



Fig. 25. Capital cost distribution of offshore wind based ammonia production plant (adapted from Ref. [13])

The utility costs are the sum of the electricity costs and the raw material costs multiplied by 1.23. The utility costs include all of the purchased electricity costs minus the revenue from the electricity. Thus, if the electricity revenue is higher than the costs, the cost of manufacture decreases. The general expenses include administration, research and development, and distribution and marketing costs. Since the electrolyzers offer unattended, continuous operation, the multiplier for the determining the general expenses from the labor costs was reduced from 19% to 10%. The multipliers for the fixed capital investment and the cost of manufacture were held at 0.9% and 16%, respectively [13].

The LCOA (levelized cost of ammonia) for the selected offshore wind based ammonia production facility is calculated to be \$1224/ton which is substantially higher than ammonia produced from a conventional natural gas based ammonia plant [13].

#### Case 6: Nuclear based ammonia production

Steam electrolysis is the primary choice for hydrogen production in nuclear based ammonia production. The efficiency is comparable to the practical efficiencies of thermochemical processes if powered by an HTGR. Steam electrolysis can be powered by a pressurized water reactor (PWR) or a boiling water reactor (BWR). Capital costs of steam electrolysis and water electrolysis differ by less than 10% [24].

Type of Reactor	Hydrogen Production Method	Efficiency (MJ Fuel/MJ <sub>Tin</sub> %)	Capital Investment Cost (million \$)	Production Cost (\$/ton)
HTGR with heat integration	Steam Electrolysis	48	1440	172
HTGR without heat integration	Steam Electrolysis	41	1570	189
HTGR	Water Electrolysis	37	1590	187
ABWR with heat integration	Steam Electrolysis	29	1540	196
ABWR	Water Electrolysis	23	1680	200

Table 30. Comparison of performance and costs of large nuclear powered ammonia plants

Source: Data from Ref. [24]

The capital investment cost and production cost of ammonia via nuclear systems are illustrated in Table 30 and Fig. 26. Nuclear based ammonia production has the lowest operating costs which corresponds to 10-20% less than partial oxidation of coal and 40-50% less than steam methane reforming process as shown in Table 31. Nuclear based ammonia production has the highest capital costs which is 65-75% more than partial oxidation of coal 400-430% more than steam reforming methane as given in Table 31.

In the ammonia synthesis loop, it is assumed that multiple intercoolers are used for compressor, ammonia reactor is at 200 bar and 20% of ammonia reactor in one cycle. Using the dissolved argon prevents excessive accumulation. In addition, for HTGR powered ammonia production system, 84% of is used for electricity, 10% is used for compressors and 6% is utilized as heat.

Process	Ammonia Production (ton/day)	Efficiency (%)	Capital Investment (million \$)	Ammonia Production Cost (\$/ton)
Natural Gas	2100	79	360	331
Natural Gas with Sequestration	2100	76.4	420	356
IRIS	1120	28.7	580	201
GTHTR	1080	41.5	700	227
Coal	2100	42.7	870	218
Coal with Sequestration	2100	39.5	1000	291
HTGR	2100	48.3	1440	172
ABWR	2100	29.4	1540	196
Wind	2100		4000	321

Table 31. Comparison of ammonia production and capital investment costs for various methods

Source: Data from Ref. [24]



Fig. 26. The capital investment cost of various ammonia production methods (data from Ref. [24])

The main advantages of nuclear powered ammonia production could be listed as follows:

- readily available raw materials air and water
- low and constant operating costs
- no co<sub>2</sub> emissions

High capital costs are the major disadvantage of nuclear powered ammonia production however, by enabling smaller and standardized modular reactors, it could be reduced the capital costs, construction cost and time, licensing cost and time [24].

High-temperature gas-cooled reactor (HTGR)-integrated high-temperature steam electrolysis (HTSE) was also considered to supply hydrogen to the ammonia process. In this scenario, coal usage for hydrogen production can be completely eliminated; hence, the process configuration is radically altered and no longer resembles the conventional coal-to-ammonia case. Two such configurations were considered in this study, and results indicate that approximately four 600 MWt HTGRs are required to support production of 3,360 ton/day of ammonia. Substituting hydrogen from water via nuclear-integrated HTSE instead of natural gas reforming or coal gasification (followed by shift conversion) eliminates fossil fuel consumption and the CO<sub>2</sub> emissions associated with these processes.



Fig. 27. HTSE based ammonia and various products synthesis from nuclear electricity (adapted from Ref. [25])

High temperature steam electrolysis (HTSE) based ammonia production method uses cryogenic air separation as the nitrogen source. Hydrogen for ammonia synthesis is produced by HTSE. Nuclear HTGRs supply heat and power for the electrolysis units [25].

Urea production requires  $CO_2$  as a feed to the process. For this case, a  $CO_2$  supply is not readily available and must be produced to support urea manufacture; hence, natural gas is burned with oxygen to produce the required  $CO_2$ . While coal could have been selected for this purpose, natural gas is preferred because of the much simpler gas cleanup requirements [25].

Fig. 27 and Fig. 28 show an example of ammonia production facility including nitric acid, urea and ammonium nitrate synthesis by utilizing the nuclear waste heat and nuclear electricity. Nuclear electricity is used for high temperature electrolysis, air separation unit, feed gases compression for ammonia synthesis and other auxiliary equipment. Nuclear heat at temperature 700°C is used as supporter for high temperature steam electrolysis process.

As HTGR technology matures and reactor outlet temperatures increase, the nuclear reactors may be able to supply electrolysis topping heat. However, because of the upper limit of 700°C deliverable heat assumed in this study, supplying topping heat from the burner to the electrolyzers is an attractive means of increasing electrolyzer efficiency [25]



Fig. 28. Inputs and outputs of the plant via HTSE to ammonia method (adapted from Ref. [24])

The proposed high temperature steam electrolysis based ammonia and derivatives production yield 2,939 ton/day urea, 3,779 ton/day ammonium nitrate, 2,435 ton/day oxygen. The required heat and electricity for the process are 222 MWt and 770 MWe, respectively.

The economic modeling calculations for HTGR technology were based on capital cost scenarios for current best estimate of US2,000/kWt where kWt is the thermal rating of the plant. In comparison, light water nuclear reactor costs are approximately US1,333/kWt. Based on the capital cost scenarios for HTGR technology, the nominal capital cost for a 600 MWt HTGR would be US1.2 billion [25].



Fig. 29. Distribution of total capital investment for a plant including urea, ammonium nitrate and nitrite acid production via HTSE ammonia production method (adapted from Ref. [25])

The total capital investment (TCI), based on the total equipment costs, annual revenues, and annual manufacturing costs were first calculated for the case. The present worth (PW) of the annual cash flows (after taxes) was then calculated for the TCI, as well as the TCI at + 50% and -30% of the HTGR cost, with the debt to equity ratios equal to 80%/20% and 55%/45%. Gas cleanup includes costs for water gas shift reactors, the Selexol process, sulfur recovery, pressure swing absorption, methanation, and CO<sub>2</sub> compression/liquefaction as appropriate for the various process configurations. The fixed capital costs were estimated from literature estimates and scaled estimates (capacity, year, and material). Finally, an engineering fee of 10% and a project contingency of 18% were assumed to determine the TCI. The capital cost provided for the HTGR represents a complete and operable system, engineering fees and contingencies were not applied to this cost. The total investment cost of this HTSE plant was calculated as US\$6,302,210,656 [25]. The results for the HTSE hydrogen cases look promising. However, integrating with nuclear power significantly increase the capital cost of the plant as seen in Fig. 29. This is due principally to the need for four nuclear reactors to support both hydrogen and electrical demands of the plant. Finally, in order to determine the most attractive options for ammonia production, various perspectives [26-31] such as life cycle, efficiency, cost and sustainability need to be addressed for the overall assessment of the selected options.

# Conclusions

The following concluding remarks are extracted from this comprehensive feasibility study covering a variety of methods, systems and applications:

- Atmospheric pressure electrolysis systems produce the hydrogen at 1 atm and then pressurizes for further usage to about 20 bar. The compression cost of hydrogen to about 20 bar is 1.03\$/kg H<sub>2</sub> which corresponds to 15% of overall cost. In order to increase the pressure to Haber-Bosch reaction temperature, more energy input are then required.
- High pressure water electrolysis system is an alternative option for reducing the required power of ammonia synthesis process by eliminating the main compressors in the system. It also reduces the cost to \$0.40 from \$1.03 (corresponding to approximately 40% after deducting the compression cost) for hydrogen production cost as compared to mechanical compression when the high pressure PEM electrolyzers are utilized.
- Hydrogen produced by using pressurized water require less power than using hydrogen compressor. The required power difference is about 15% which brings lower cost hydrogen and ammonia.
- Producing ammonia directly from high pressure electrolysis near the ammonia production facility eliminates the compression, storage and delivery processes of hydrogen which brings down the overall ammonia production cost.
- For standard central water electrolysis with an electricity price of 3.7 US¢/kWh, plant gate hydrogen production is calculated to be 3.2 \$/kg although it is 5.6 \$/kg for dispended hydrogen.
- The lowest average electricity price in Canada for large-power customers is observed in Winnipeg, Edmonton and Calgary with 3 US cent/kWh, 3.2 US cent/kWh and 3.60 US cent/kWh, respectively.
- The lowest cost of high pressure electrolysis based hydrogen is calculated to be 3.8 US cent/kg at 2787 mA/cm<sup>2</sup> current density for 3.5 US cent/kWh electricity price resulting in 0.76 US \$/kg ammonia end product price.
- In total, the capital cost of 250 ton N<sub>2</sub>/day air separation plant corresponds to 6,922,430 \$ which is only 3% of overall ammonia production plant cost.
- The excess heat in Haber-Bosch reactor can be utilized for liquid nitrogen vaporization and liquefied natural gas vaporization in order to decrease mechanical compression costs.
- Nearly 65% of overall capital cost of 300 ton/day ammonia production plant comes from electrolyzer.
- Thermal plasma disassociation of methane is an alternative option for hydrogen production which brings approximately 20% less power input for 300 ton/day ammonia production plant. However, the effect of high pressure on plasma disassociation of methane needs to be further studied.
- In thermal plasma disassociation of methane, carbon black is also obtained as a valuable product for various industries which can be sold about 0.9-1 US\$/kg.
- In thermal plasma disassociation option, the production of liquefied natural gas should also be included in feasibility and cost studies in order to compare the overall performance.
- When carbon black sales are considered, the cost of ammonia can decrease down to 0.42 \$/kg which is quite lower than other methods. Therefore, in any cases, producing by products may bring higher revenues and therefore lower ammonia costs.

- If 60 US\$/ton profit from ammonia trade is considered, pumped storage hydro plant yearly profit would be nearly same with a 300 ton/day ammonia production plant profit. However, the capital installation cost of pumped storage hydro plant is nearly twice of ammonia plant.
- The offshore wind based ammonia is also an environmentally friendly solution for ammonia production however, the unit cost for ammonia is still higher.
- Nuclear based ammonia production options appear to be cost competitive than other methods however the initial investment costs are much higher. High capital costs are the major disadvantage of nuclear powered ammonia production however, by enabling smaller and standardized modular reactors, it could be reduced the capital costs, construction cost and time, licensing cost and time.
- Mature Haber-Bosch technology would be optimized using liquid pumping instead of feed gases compression, high pressure electrolysis and vaporization via excess heat of Haber-Bosch reactor.

## Nomenclature

F	Faraday constant
h	Specific enthalpy (kJ/kg)
Н	gross head (m)
HHV	Higher heating value (kJ/kg)
m	Mass (kg)
ṁ	Mass flow rate (kg/s)
Ν	Number
Ν	Polytrophic exponent
Р	Pressure (bar)
Q	Heat rate (kW)
Q	Volumetric flow rate $(m^3/s)$
R	Universal gas constant (8.314 kJ/kmol K)
S	Specific entropy (kJ/kg K)
Т	Temperature (°C)
v	Specific volume (m <sup>3</sup> /kg)
V	Volume (m <sup>3</sup> )
Ŵ	Work rate (kW)
Z	Number of electrons

## **Greek letters**

η	Efficiency
$\eta_s$	Isentropic efficiency
•	Dangity (1/g/m <sup>3</sup> )

ρ Density (kg/m<sup>3</sup>)

## Acronyms

AC	Alternating current
ABWR	Advanced boiling water reactor
ASU	Air separation unit
BWR	boiling water reactor
С	Compressor

CCS	Carbon capture storage
DC	Direct current
DOE	Department of energy
DFMA	Design for manufacture and assembly
FRP	Fiber reinforced composite piping
GGE	Gasoline gallon equivalent
HP	High pressure
HTGR	High temperature gas cooling reactor
HTSE	High temperature steam electrolysis
IRIS	International reactor innovative and secure
GHG	Greenhouse gas
GTHR	Gas Turbine High Temperature Gas-cooled Reactor
HB	Haber-Bosch
LNG	Liquefied natural gas
MEA	Membrane electrode assembly
O&M	Operation and maintenance
PEM	Proton exchange membrane
PW	Present worth
PWR	Pressurized water reactor
RF	Radio frequency
SMR	Steam methane reforming
STP	Standard temperature and pressure
UCG	Underground coal gasification
TCI	Total capital investment

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## **APPENDIX 1: PROGRESS REPORT 1 (MAY-AUGUST 2015)**



# Comparative assessment of NH<sub>3</sub> production and utilization in transportation systems for

Ontario

Application Ref. IT05701 Funding Request Ref.FR11885 Invoice Ref. 1516-10898 Mitacs File: ON – IRDI

**Progress Report 1** 

Period: May-August 2015

## Summary

The present progress report provides various ammonia production methods, ammonia utilization opportunities in transportation sector, comparative life cycle assessment of ammonia production techniques and ammonia vehicular applications. Ammonia production methods from conventional sources to renewable sources are investigated. A comparison of ammonia usage in transportation sector is also provided. Using SimaPro software, detailed life cycle analyses of various ammonia production methods are performed.

The results of the present progress report fulfill following project objectives:

- An extensive study on the ammonia production from various types of resources such as renewable energies (wind, solar), methane steam reforming and excess power in nuclear and/or hydro power plants. Assess the emissions and pollutants discarded by each method during processes.
- Identification of opportunities for green NH<sub>3</sub> production and efficient utilization of ammonia in various sectors and especially in transportation sector.
- A life cycle analysis of ammonia production methods and impact of ammonia production on environment.

# Introduction Hydrogen production

The hydrogen is produced by using various methods as shown in the Figs.1-3. Based on process type there are two main routes: Thermal and electrical. The most common fossil fuel based methods use the methane, coal or hydrogen sulphide as feedstock as well as energy source. The Steam methane reformation is one of the most common routes considered for hydrogen production [1,2] and eventually ammonia production. Second way is splitting water using thermal or electrical energy. The electrolysis when assisted with heat is called high temperature electrolysis. The electrolysis can be based on renewable sources as photo voltaic or wind based electrolysis. Only heat is used for water splitting in pure thermal processes. Direct splitting of water requires very high temperature and very inefficient process, therefore catalysts are used to assist the splitting that reduce the temperature required for the process and pave the way of utilization of heat rejected by power plants or solar energy based systems [3-6].



Fig.1. Hydrogen production based on fossil fuels



Fig.2. Hydrogen production based on thermal water splitting



Fig.3. Hydrogen production by water electrolysis

#### **1.2 Ammonia production**

Ammonia is considered not only as a feedstock but also proposed as an energy carrier. Due to its many advantages over hydrogen it can be a medium to store and carry energy.

More than 90% of the world ammonia production currently uses the Haber-Bosch synthesis process, which is named for Fritz Haber and Carl Bosch who developed the process in 1913 [7, 8]. This method is based on combining hydrogen and nitrogen over an iron oxide catalyst. In order to increase the performance of the plants, Haber-Bosch synthesis has been performed with different variations in synthesis pressure, temperature, and catalysts. However, new technologies such as thermochemical and solid state synthesis processes are currently being developed to further decrease the cost and improve the efficiency of ammonia production.

Note that natural gas is the primary feedstock used for producing ammonia in Canada, and worldwide. There are 11 ammonia plants operating in Canada, producing an average of 4–5 million metric tonnes annually per plant [9]. Canadian ammonia plants recover a high percentage of process generated CO2 (~40%) to produce urea, and have the highest feed-plus-fuel energy (FFE) plant efficiency internationally [9]-consuming an average of 33.8 GJ/tonne NH3 for natural gas plants, compared to the international average of 38.6 GJ/tonne NH3.

Ammonia one of the largest produced industrial chemical in the world (in 2012 - tonnage 198 million). Ammonia production consumes almost 1.2% of total primary energy and contributes 0.93% of GHGs [10]. Approximately 1.5 tons of CO2 is emitted to the atmosphere during the production of 1 ton of ammonia [11].



Fig.4. World ammonia production increase (Data from Ref. [12])



Fig.5. Worldwide ammonia production amounts by country (Data from Ref. [13])

A detailed economical and electrical consumption comparison of ammonia production techniques was prepared in Ref. [14] as tabulated in Table 1.

[14])							
Production Method	Fuel	Energy (GJ/t NH3)	Emissions (t CO2eq/t NH3)	\$/t NH3	Details		
Steam- methane reforming	Natural gas (CH4)	38.6 (33.8b)	1.8	400 - >1000	most common method - fossil fuel derived - highly unstable price		
Gasification	Coal	54	4.6	150 - 425	<ul> <li>predominantly used in China</li> <li>high energy and emission intensity</li> </ul>		
H2O Electrolysis +Haber Bosch	electricity (hydro)	12 GWh	0	255 – 735	- electricity may be produced from any energy resource, including renewable		
Solid state ammonia synthesis (SSAS)	electricity (hydro)	7.5 GWh	0	140 – 440	<ul> <li>proton conducting membrane reactor</li> <li>eliminates electrolysers and Haber-Bosch process</li> </ul>		

Table 1. Economical and electrical comparison of ammonia synthesis processes (Data from Ref.

In terms of conventional resources, naphta, heavy fuel oil, coal, natural gas coke oven gas and refinery gas can be used as feedstock in ammonia production. Globally, 72% of ammonia is produced using steam reforming of natural gas. Steam methane reforming method is currently least energy intensive technique among others. In China, coal is intensively used and is generally characterized by high energy intensities. Natural gas costs are 70-90% of the production cost of ammonia. Since, ammonia production is based on natural gas in SMR method, if natural gas prices rise, production costs for ammonia increase in parallel. [15, 16].



Fig.6. Sources of Ammonia production based on feedstock use (Data from Refs. [15,16])

Furthermore, ammonia production methods are more intensively emphasized and analyzed in the section 2.

### **1.3 Ammonia transportation**

Ammonia gas is very soluble in water. At ambient temperature and atmospheric pressure, ammonia is an alkaline, colourless gas with a pungent and suffocating odour. Substantial, storage and delivery systems are already available for NH3 used in fertilizer applications. NH3 has been transported by ship, barge, rail car, truck, and pipeline for decades. It is in the top three chemicals transported annually. Large capacity which corresponds to 20,000 to 30,000 tons and low cost NH3 storage tanks are currently installed in many parts of the USA [17].

Most economical transport method is pipelines. Therefore long distance transport of ammonia is classically held by using pipelines [18]. 4,830 km carbon steel pipeline network is already used in the US to transport ammonia from port and production facilities to agricultural areas for use as a fertilizer. There are currently storage services and terminals located along the pipeline to support operations. In Iowa, there are more than 800 ammonia retail places [e.g., 17].

Property	Liquid		
Colour	Colourless		
Density (0°C, 101.3 kPa)	638.6 kg/m3		
Density (-33.43°C, 101.3 kPa)	682 kg/m3		
Boiling point (101.3 kPa)	-33.43°C		
Melting point	-77.71°C		
Critical temperature	132.4°C		
Critical pressure	11.28 MPa.		
Critical viscosity	23.90 x 10-3 mPa.s		
Lower heating value, LHV (MJ/kg)	18.57		
Higher heating value, HHV (MJ/kg)	22.54		

Table 2. Properties of ammonia (Data from Ref.[19])



Fig.7. Ammonia transportation pipelines in USA (Data from Ref.[20])

Note that pressurized NH<sub>3</sub> storage and delivery infrastructure are very similar in design and performance to propane (LPG) delivery infrastructure, because they are both compressed liquids at moderate pressure. The significant, proven, worldwide availability of propane fueled vehicles and furnaces, provides a familiar example of how ammonia fuel systems would appear physically. An ammonia pipeline from the Gulf of Mexico to Minnesota and with branches to Ohio and Texas has served the NH3 industry for several decades. Since ammonia can be shipped and stored in mild

steel pipelines, any natural gas or petroleum pipeline could be cost-effectively converted to carry NH<sub>3</sub>. This brings an important advantage. Currently, there are nearly two million miles of natural gas pipeline in the U.S.A. This pipelines could be converted to carry NH<sub>3</sub>, making NH<sub>3</sub> fuel readily available to nearly every community in the U.S.A. A pipeline of a given size can deliver nearly 50% more energy when transporting liquid NH3 than if it is used to deliver compressed natural gas. A 50% increase in energy delivery capacity denotes a massive cost savings and energy savings [21].

#### 1.4 Ammonia utilization

The ability to use one fuel in all types of combustion engines, gas turbines, burners and directly in efficient fuel cells is a tremendous advantage. Storage and delivery infrastructure would be greatly simplified, far fewer fuel formulations would be required and would be easier to produce to a given standard, refueling stations would be standardized and lower in cost. NH<sub>3</sub> is one of a very short list of fuels that can be used in nearly every type of engine and gas burner with only modest modifications. Gas burners can be equipped with in-line partial reformers to split approximately 5% of the NH<sub>3</sub> into hydrogen. This mixture produces a robust, unpolluted burning open flame. One pipeline to a home could provide NH<sub>3</sub> to furnaces/boilers, fuel cells, stationary generators and even vehicles. Due to the very minor enthalpy of reforming exhibited by NH<sub>3</sub> it can easily be reformed to hydrogen for any application that would require hydrogen. Relatively minor modifications allows efficient use of ammonia as a fuel in diesel engines; high compression ratio spark ignition engines can produce astounding efficiencies of over 50% using NH<sub>3</sub> fuel; direct ammonia fuel cells promise to be low-cost, robust and very efficient; NH<sub>3</sub> is also a very suitable fuel for use in solid oxide fuel cell and gas turbines. These medium-temperature (approximately 400°C) fuel cells promise to be low-cost (due to low-cost catalysts and packaging), highly efficient and very robust. [21].



Fig.8. World ammonia consumption (Data from Ref.[22])

Global ammonia demand is forecasted to grow at an average annual rate of approximately 3% over the next five years. The historical growth rate was 1%. Therefore, currently it is 2% above. Robust agricultural fundamentals are expected to drive this growth as fertilizer uses account for approximately 80% of global ammonia demand [22].



Fig.9. World ammonia trade (Data from Ref. [23])



Fig.10. Domestic and export based world ammonia production profile (Data from Ref. [24])



Fig.11. Ammonia consumption in USA for industrial and fertilizer purposes (Data from Ref. [25])

The physical properties of ammonia require high-pressure containers, making it costly and difficult to transport. As a result, most of ammonia is consumed close to where it is produced.



Fig.12. World ammonia usage, average of 2010-2013 (Data from Ref. [26])

The USA is recognized as the largest ammonia importer and typically accounts for approximately 35-40% of world trade. Europe, a higher-cost producer, accounts for roughly 25% of trade. The majority of growth in imports is expected in Asian countries, for indurial uses and for the production of fertilizer products.



Fig.13. Comparison of various fuels in terms of energy density, HHV and cost (modified from Ref. [27])

As seen in Fig.13. ammonia has lowest cost per GJ compared to conventional fuels such as gasoline and CNG, respectively.

### **Ammonia production**

Although there are a few methods for ammonia synthesis, commonly two different ammonia synthesis techniques are available in the world namely; Haber-Bosch process and solid state ammonia synthesis process as illustrated in Fig.14. In both methods, nitrogen is supplied through air separation process mainly as cryogenic. Cryogenic air separation is currently the most efficient and cost-effective technology for producing large quantities of oxygen, nitrogen, and argon as gaseous or liquid products [28]. Cryogenic technology can also produce high-purity nitrogen as a useful by product stream at relatively low incremental cost. Among other air separation processes, cryogenic air separation has most mature and developed technology. Since ammonia is produced at high amounts, required nitrogen should be produced in a low cost and high efficient manner which corresponds to cryogenic air separation. Therefore, in the life cycle analysis, cryogenic air separation method is utilized. Required electricity could be supplied either from conventional or alternative sources.



Fig.14. Ammonia production methods via conventional and renewable sources

The Haber process is the most common method to produce ammonia [1]. It is an exothermic process that combines hydrogen and nitrogen in 3:1 ratio to produce ammonia. The reaction is facilitated by catalyst and the optimal temperature range is 500-600 °C [2, 3]. In Haber-Bosch process shown in Fig.15, the impact of ammonia production basically depends on the methods used to produce hydrogen and nitrogen. In the next section, various methods of hydrogen and ammonia production are illustrated.

The nitrogen and hydrogen gas mixture is compressed to 120-220 bar, depending on the particular plant, before it enters the ammonia synthesis loop [29]. Only a portion of the mixture gas is converted to ammonia in a single pass through the converter due to thermodynamic equilibrium of the ammonia synthesis reaction. The residual unreacted gas is passed through the converter again, creating a flow loop for the unreacted gas. The gaseous ammonia and unconverted mixture gas then enters the ammonia recovery portion of the synthesis loop. Refrigeration coolers decrease the temperature of the gas to -10°C to -25°C so that the ammonia condenses out of the mixture, thus leaving behind the unreacted synthetic gas [30].

Impurities in the mixture gas from the steam reformation process, such as argon from the air and methane from the methanation process, are then removed from the mixture. Makeup nitrogen/hydrogen mixture gas is then added to the synthesis loop and combined with the

remaining unconverted mixture gas from the cooler. Since the gas is scattered through the synthesis loop by using a compressor, efforts are made to maintain a low pressure drop in the synthesis loop.

Conversion to ammonia (10–15%) is thermodynamically limited ending up with serious disadvantages of Haber Bosch process [31]. In addition, environmental contamination is severe and energy consumption is high [32, 33]. The Haber Bosch process lasts to be improved, mostly through changes in the catalyst and heat recovery. One catalytic improvement that is starting to be used commercially is a ruthenium-based catalyst instead of an iron-based catalyst [34]. An improved catalyst allows more ammonia to be produced per pass through the converter at lower temperatures and pressures.



Fig.15. Ammonia production via Haber Bosch process

The other developing ammonia production method is solid state ammonia synthesis (SSAS). The system uses a solid state electrochemical process to produce ammonia from nitrogen, water, and electricity.

In SSAS, a proton-conducting membrane is heated to about 550°C. Nitrogen is supplied to one side of the membrane and water vapor is supplied to the other side, under conditions of equalized pressure to drive the reaction. The water vapor separates into protons and oxygen, an external voltage drives the protons through the membrane, and the nitrogen and protons react on the nitrogen side of the membrane to form NH<sub>3</sub>. The lower energy consumption of the SSAS process suggests that it will be able to produce ammonia at a lower cost than the Haber-Bosch process, with the obvious environmental advantage of not using fossil fuel feedstock.

SSAS process requires 7,000-8,000 kWh/ton-NH<sub>3</sub>, compared to 12,000 kWh/ton-NH<sub>3</sub> for an electrolyzer with a Haber-Bosch synloop [35]. The capital cost is roughly 200,000 \$/ton-day-

NH3, which is significantly less than the 750,000 \$/ton-day-NH<sub>3</sub> estimate for an electrolyzer with a Haber-Bosch synloop system.

The SSAS technology is preferably well-matched for renewable energy sources that produce electricity, such as wind and solar photovoltaic, since the electrolyzers for hydrogen production and the Haber-Bosch synloop are abolished with the SSAS system, resulting in numerous energy and economic benefits [35]. In this regard, the schematic diagram of SSAS process is illustrated in Fig.16.



Fig.16. Ammonia production via Solid State Ammonia Synthesis

For the Haber Bosch process, production of ammonia is based on various hydrogen production techniques as shown in Fig.17. In contrast, in SSAS process, it is based on generating super-heated steam as illustrated in Fig.18.



Fig.17. Ammonia production and usage routes by the Haber Bosch process



Fig.18. Ammonia production and usage routes through SSAS process

#### **1.5 Ammonia Production Methods**

#### 1.5.1 Steam Methane Reforming

Most common process for hydrogen production. Most efficient and cost effective process. Adverse impact on environment, uses fossil fuel as feed stock.

The production of ammonia from natural gas begins by producing hydrogen and nitrogen for the ammonia synthesis process. The natural gas is first cleaned by using a hydrodesulfurization process to remove the small amount of sulfur contained in the gas, which would damage the catalyst in the ammonia synloop. This process injects a small amount of hydrogen into the natural gas and then heats the gas to 400°C over a cobalt oxide or nickel oxide catalyst. Hydrogen sulfide is formed and then removed over a bed of zinc oxide to produce zinc sulfide and water. Steam is then added to the sulfur-free natural gas to preheat the gas and to create a steam-to carbon molar ratio of between three and four. The mixture then enters the primary reformer, which is a furnace with a nickel oxide catalyst, at a pressure of 25-40 bar. The reactants are heated to 750-850°C to provide the heat needed for the endothermic methane-steam reaction [36]. The mixture then enters the secondary reformer where air, which is compressed and preheated, is added. The oxygen from the air reacts with the hydrogen to raise the temperature in the reformer to 1,000°C, which further shifts the equilibrium of the methane steam reaction to decrease the methane content to about 0.3% on a dry basis [36]. The amount of air added is controlled to provide a molar ratio of three hydrogen to one nitrogen, which is needed to produce ammonia. The gas is cooled and used to generate steam before entering the shift conversion stage where the CO shift reaction is used to decrease the amount of carbon monoxide in the mixture. At lower temperatures, the equilibrium mixture shifts to produce carbon dioxide and hydrogen from the carbon monoxide and water entering the shift conversion reactor.

Two stages are typically used, beginning with an iron oxide and chromium oxide catalyst at 350-500°C and followed by a copper oxide, zinc oxide, and alumina catalyst at 200-250°C [36]. Following this process, the carbon monoxide content of the gas is reduced to about 0.3% on a dry basis [36]. The carbon dioxide in the mixture is then removed to a level of less than 0.1% by using either the Benfield, Selexol, or MDEA process. The remaining trace amounts of carbon oxides (CO, CO<sub>2</sub>) are then removed through methanation, which is where a nickel oxide catalyst at 250-350°C converts the carbon oxides to methane by using some of the hydrogen gas in the process. After this stage, less than 5 ppm of carbon oxides remain in the mixture, which is important to minimize problems with oxygen damaging the catalyst in the ammonia synthesis loop [36]. The mixture is then cooled to condense out the water and to capture heat. The nearly pure mixture of hydrogen and nitrogen is then pressurized as it enters the synloop, where the gas is converted into ammonia.



Fig.19. Ammonia production via steam methane reforming

## 1.5.2 Coal Gasification

There are mainly two type of coal gasification. The one is called as underground coal gasification which take place below earth level and the other one is coal gasification which takes place above earth level. The second most commonly used process for hydrogen production. With depletion of oil and gas resources the dependence on coal will increase substantially [1].



Fig.20. Ammonia production via underground coal gasification with CO<sub>2</sub> capture

Coal gasification is used to produce synthetic gas as the input to the Haber-Bosch process. This gasification process involves an exothermic reaction of coal with a mixture of oxygen and steam to produce synthetic gas, mainly consisting of carbon monoxide and hydrogen [34].



Fig.21. Ammonia production via underground coal gasification without CO<sub>2</sub> capture

Important capacities of water, carbon dioxide, and methane can also be found in the synthetic gas products. The synthetic gas is processed by using the methane-steam reaction and CO shift reaction to shift the carbon monoxide and methane into hydrogen. The gas also goes

through several treatments to remove carbon dioxide and trace substances in the gas stream, such as particulates and sulfur and nitrogen compounds [37]. The hydrogen and nitrogen mixture is then fed to the Haber-Bosch synloop for production of ammonia.



Fig.22. Ammonia production via coal gasification

# 1.5.3 Biomass Gasification

The biomass gasification process provides a reliable and credible alternative and one of the fastest growing renewable technologies.



Fig.23. Ammonia production via biomass downdraft gasification




## 1.5.4 Solar PV Based Electrolysis

Solar PV is being accepted as credible alternative to fossil fuels based distributed energy systems. Though PV is renewable source but it has large environmental impact due to panel production and battery usage. Therefore LCA can be used to assess the overall environmental impacts of ammonia production using photovoltaic technology.



Fig.25. Ammonia production via solar energy based electrolysis

#### 1.5.5 Ammonia from Ocean Thermal Energy Conversion

An Ocean Thermal Energy Conversion (OTEC) is a solar based energy source utilizing the temperature difference between the ocean surface and deep ocean waters. Near the equator, solar energy warms the top 50-100 m of ocean to a temperature of 27-30°C while ocean water at a depth of 1,000 m remains at or below 5°C [38]. To extract the energy, a vapor-power cycle is constructed by using the hot and cold heat reservoirs of ocean water. Warm surface water is passed through a heat exchanger to boil a liquid with a low boiling point, such as ammonia, propane, or fluorocarbons, which is then passed through a turbine to drive an electric generator, similar to a conventional steam Rankine cycle power plant. The fluid leaving the turbine is condensed in another heat exchanger by using the cold water extracted from deep in the ocean. To repeat the cycle, the condensed working fluid is pumped back to the first heat exchanger where the warm ocean surface water once again boils the liquid for use in the turbine.

The advantage of using OTEC is the constant availability of the renewable resource during each and every day and hour of the year, unlike other renewable energy resources, such as wind and solar, which tend to have a cyclical and unpredictable nature of energy production. One of the complications with OTEC power generation is the transportation of the energy generated to the end users. Storing the generated energy in chemical form, such as ammonia, may help solve this problem and make the technology feasible. It was suggested such a design in 1985, consisting of a 325 MW net electrical output OTEC plant producing ammonia at a rate of 1,000 t/day [38]. The plant would distill and electrolyze sea water to produce hydrogen that can then be combined with nitrogen, separated from air, to make ammonia. The ammonia would then be cooled and stored onboard the OTEC plant before being transported to land via tankers and used as either a transportation fuel or in the ammonia fertilizer industry [38]. The technology to construct a commercial power plant was verified in a test of MINI-OTEC in 1979 near Keahole Point, Hawaii. MINI-OTEC was a small, closed loop system that used ammonia as the working fluid, and in addition, was the first at sea plant to produce net power. The plant generated 50 kW of electrical energy during operation. However, it consumed 21.3 kW to power the seawater pumps, although additional losses in the system reduced the net power output to 17.3 kW [39]. The proposed 1,100 t/day, 365 MW full-scale plant would provide the motor vehicle fuel equivalent of 150,000 galgasoline/day. Approximately 2,000 of these plants would be needed to supply all of the energy needed by automobiles in the United States, which would result in a OTEC facility spacing of 175 km throughout the tropical ocean [40]. The MINI-OTEC plant produced little power; however it did prove the concept of using OTEC to generate a net amount of electricity. The ability of OTEC to produce a net amount of power was further supported in a paper by Avery et al. in 1999, which stated that a 46 MW pilot plant needs to be built to further test full scale feasibility [40].



Fig.26. Ammonia production via ocean thermal energy based electrolysis

#### 1.5.6 Wind Energy Based Electrolysis:

Wind contributes more than 20% of total renewable electricity produced worldwide. This promotes distributed (onsite) generation, reduces the cost of transportation. The system considered for producing hydrogen from wind energy involves two main devices: a wind turbine that produces electricity, which in turn drives a water electrolysis unit that produces hydrogen. Wind energy is converted to mechanical work by wind turbines and then transformed by an alternator to alternating current (AC) electricity, which is transmitted to the power grid. The efficiency of wind turbines depends on location, with wind energy applications normally making sense only in areas with high wind activity [41]

Wind to ammonia systems produce ammonia through the use of electricity from wind turbine generators, which are usually large horizontal-axis wind turbines mounted on a tower. Wind turbines are commercially available in sizes up to about 2.5 MW of nameplate capacity for on-shore applications and even larger machines can be found in off-shore applications. The electrical output of the wind turbine is highly dependent on wind speed, resulting in a high variability in electrical energy production. The basic ammonia synthesis design is to use an electrolyzer to produce hydrogen from water and an air separation unit to obtain nitrogen from air, both of which are combined in a Haber-Bosch synthesis reactor for production of ammonia [42]



Fig.27. Ammonia production via wind energy based electrolysis

#### 1.5.7 Partial oxidation of heavy oils

The partial oxidation process is used for the gasification of heavy feedstocks such as residual oils and coal. Exceedingly viscous hydrocarbons and plastic wastes may also be used as fractions of the feed. An air separation unit is required for the creation of oxygen for the partial oxidation step. The nitrogen is added in the liquid nitrogen wash to remove impurities from the synthesis gas and to get the required hydrogen/nitrogen ratio in the synthesis gas. The partial oxidation gasification is a non-catalytic process taking place at high pressure (>50bar) and temperatures about 1,400°C. Some steam is added for temperature moderation.

The partial oxidation process offers an alternative for future utilisation of such wastes. Carbon dioxide, methane and some soot are formed in addition. The sulphur compounds in the feed are converted to hydrogen sulphide. Mineral compounds in the feed are transformed into specific ashes. The process gas is freed from solids by water scrubbing after waste heat recovery and the soot is recycled to the feed. The ash compounds are drained with the process condensate and/or together with a part of the soot. In at least two units in Europe, the soot is separated from soot water in a mainstream filtration stage, to avoid ash build-up in the gasification cycle downstream units. The heavy metals, such as V, Ni and Fe are recovered. The hydrogen sulphide in the process gas is separated in a selective absorption step and reprocessed to elementary sulphur in a Claus unit.

The shift conversion usually has two high temperature shift catalyst beds with intermediate cooling. Steam for the shift conversion is supplied partially by a cooler-saturator system and partially by steam injection. CO2 is removed by using an absorption agent which might be the same as that in the sulphur removal step. Residual traces of absorption agent and CO2 are then removed from the process gas, before final purification by a liquid nitrogen wash. In this unit practically all the impurities are removed and nitrogen is added to give the stoichiometric hydrogen to nitrogen ratio. The ammonia synthesis is quite similar to that used in steam reforming plants, but simpler and more efficient, due to the high purity of synthesis gas from liquid nitrogen wash units and the synthesis loop not requiring a purge [43].



Fig.28. Ammonia production via nuclear energy based electrolysis

Thermochemical cycles, and electrolysis processes will require a primary energy source capable of supplying electrical (for electrochemical processes) and thermal energy. One main energy source for these production techniques is nuclear energy [44]. However, existing nuclear power plants in the United States and elsewhere are typically water cooled plants operating at 500–750 K. Advanced designs are being considered for nuclear power plants operating at significantly higher temperatures that correspond to the temperature requirements of the electrolytic or thermochemical water-splitting process. For example, the gas-cooled fast reactor (GFR) is capable of providing thermal energy at temperatures of 1100 K. Another alternative is the very-high temperature reactor (VHTR) system capable achieving a temperature of 1250 K [45].



Fig.29. Ammonia production via geothermal energy based electrolysis

### 1.5.10 Hydroelectric based electrolysis



Fig.30. Ammonia production via hydroelectric based electrolysis

1.5.11 Tidal and wave energy based electrolysis



Fig.31. Ammonia production via tidal and wave energy based electrolysis

#### 2. Case studies

Life cycle assessment (LCA) is essentially a cradle to grave analysis to investigate environmental impacts of a system or process or product. The concept of exergetic LCA has only begun to be introduced into the LCA approach [46].

LCA is a methodology for this type of assessment, and represents a systematic set of procedures for compiling and examining the inputs and outputs of materials and energy, and the associated environmental impacts, directly attributable to the product or service throughout its life cycle. A life cycle is the interlinked stages of a product or service system, from the extraction of natural resources to final disposal [47]. LCA is a method used to help engineers, scientists, policy makers and others to assess and compare energy and material use, emissions and wastes, and environmental impacts for a product or process. The method can be used to evaluate the total environmental impact of a product or process. Overall environmental impact cannot be assessed by examining only operation, but must consider all the life stages from resource extraction to disposal during the lifetime of a product. LCA can also be conducted to compare impacts for competing products or processes. In addition, LCA can identify critical phases where process changes could significantly decrease impacts [48].

Performing an LCA allows one to:

- Quantify environmental releases to air, water, and land in relation to each life cycle stage and/or major contributing process
- Evaluate systematically the environmental consequences associated with a given product or process
- Assist in identifying significant shifts in environmental impacts between life cycle stages and environmental media
- Assess the human and ecological effects of material and energy consumption and environmental releases to the local community, region, and world
- Compare the health and ecological impacts of alternative products and processes
- Identify impacts related to specific environmental areas of concern
- Analyze the environmental trade-offs associated with one or more specific products/processes to help gain stakeholder (region, community, etc.) acceptance for a planned action

Within an LCA, mass and energy flows and environmental impacts related to plant construction, utilization, and dismantling stages are accounted for. The determination of all input and output flows is often a very complicated task, so simplifications and assumptions are often made to facilitate LCA. The challenge is to ensure the assumptions and simplifications (e.g., simplified models of processes) retain the main characteristics of the actual system or process being analyzed.

The LCA process is a systematic, phased approach and consists of four components: goal definition and scoping, inventory analysis, impact assessment, and interpretation. Goal Definition and Scoping defines and describes the product, process or activity. It establishes the context in which the assessment is to be made and identifies the boundaries and environmental effects to be

reviewed for the assessment. Inventory Analysis identifies and quantifies energy, water and materials usage and environmental releases (e.g., air emissions, solid waste disposal, waste water discharge).

Impact Assessment assesses the human and ecological effects of energy, water, and material usage and the environmental releases identified in the inventory analysis. Interpretation evaluates the results of the inventory analysis and impact assessment to select the preferred product, process or service with a clear understanding of the uncertainty and the assumptions used to generate the results. The entire system is examined in order to evaluate the impacts and choose the best option. The system must be defined so that the entire lifecycle is included, or important effects may be neglected. The procedures for performing the inventory part of an LCA have been very well defined by such groups as the Society of Environmental Toxicology and Chemistry (SETAC) and the International Organization for Standardization (ISO) [49, 50]

LCA is mainly carried out based on the input energy and flow material in the system while it's entire life cycle [51]. It is essential to set a boundary of system. LCA is a four-step process. The steps are shown in the following figure and the interpretation step is linked to all four steps, it indicates that it's a feedback system and preceding steps results can be used to improve the previous step.



Fig.32. Framework of life cycle assessment

The four steps are explained as:

#### 2.1 Life cycle assessment (LCA) : Goal and Scope Definition

This is the first step of an LCA study. This step defines the objectives of study and also the range of activities under investigation. The utmost care and detail is required to define the goals and scope of study. The LCA is an iterative process, therefore the feedback consideration should be

kept in definition of systems. Normally drawing boundary and the energy indicates the scope and materials are considered for the processes falls within these boundary limits.

# **3.2 Life Cycle Inventory Analysis**

In this step, raw material and energy, the emissions and waste data is collected. This data is used to calculate the total emissions from the system. The mass and energy balance are used at each step to calculate the life cycle inventory of the system. The life cycle inventory needs to include every possible energy and material input and all possible emissions to establish credible results. Data quality is important aspect of LCA and during inventory analysis the standards are followed for maintaining the data quality.

# 3.3 Life cycle impact assessment

The thirst step of LCA is Life cycle impact assessment. This step assesses the impacts of activities under investigation. The LCI data is utilized to find out the affected areas. The goal and scope definition sets the depth of study, impact categories in impact assessment. The LCI data is analyzed in a two steps process:

*Classification:* The Impact categories are established and LCI data is analyzed to mark the data and calculate the values of emissions corresponding to each category. The impact categories are based on the evaluation method utilized for example few of categories are Global Warming Potential (GWP), Acidification, Human Toxicity etc.

*Characterization:* It is the second step of assessment. Classification step group the data in respective impact categories and characterization step is used to evaluate the relative contribution of each type of emission to these impact categories.

*Normalization and Weighting:* This step is not mandatory and used sometimes, the emissions are normalized corresponding to a standard and converted into a score system. The total score is utilized to identify the methods and processes of concern.

# 3.4 Interpretation of Results and Improvement

The last step is interpretation of results and feedback for improvement of system. The gray areas of system are identified and highly polluting processes can be eliminated with cleaner alternatives.

# 3.5 Assessment Methods

There are a number of assessment methods evolved over the time to classify and characterize the environmental flows of system, a few are Eco-indicator 99, EDIP 2003, CML 2001, IMPACT 2002+, ReCiPe Endpoint, CML 2 baseline 2000, BEES, TRACI 2, EDIP 2. The two methods used for the present analysis are CML 2001 and Eco-indicator 99.

# 3.5.1 CML 2001 Method

# 3.5.1.1 Depletion of Abiotic Resources

The main concern of this category is the human and ecosystem health that is affected by the extraction of minerals and fossil as inputs to the system. For each extraction of minerals and fossil

fuels, the Abiotic Depletion Factor (ADF) is determined. This indicator has globe scale where it is based on concentration reserves and rate of de-accumulation.

# 3.5.1.2 Human Toxicity

Toxic substances on the human environment are the main concerns for this category. In the working environment, the health risks are not included in this category. Characterization factors, Human Toxicity Potentials (HTP), are calculated with USES-LCA, describing fate, exposure and effects of toxic substances for an infinite time horizon. 1,4-dichlorobenzene equivalents/ kg emissions is used to express each toxic substance. Depending on the substance, the geographical scale varies between local and global indicator.

# 3.5.1.3 Fresh Water Aquatic Eco-Toxicity

This indicator considers the impact of the emissions of toxic substances to air, water, and soil on fresh water and ecosystems. USES-LCA is used to calculate the Eco-toxicity Potential by describing fate, exposure and effects of toxic substances. 1,4-dichlorobenzene equivalents/kg emissions is used to express infinite Characterization factors which is the time horizon. The scale of this indicator can be applied to global/continental/ regional and local scale.

# 3.5.1.3 Acidification potential

Acidifying substances causes a wide range of impacts on soil, groundwater, surface water, organisms, ecosystems and materials. RAINS 10 model is used to calculate the Acidification Potential (AP) for emissions to air, describing the fate and deposition of acidifying substances. SO2 equivalents/ kg emission is used to expresses the AP. This category has a different geographical scale that can be local and global. Depending on the availability the Characterization factors including fate were used. However, when not available, the factors used without fate (In the CML baseline version only factors including fate were used). The method was extended for Nitric Acid, soil, water and air; Sulphuric acid, water; Sulphur trioxide, air; Hydrogen chloride, water, soil; Hydrogen fluoride, water, soil; Phosphoric acid, water, soil; Hydrogen sulphide, soil, all not including fate. Nitric oxide, air (is nitrogen monoxide) was added including fate

## 3.5.1.4 Global Warming

The greenhouse gases to air are related to the Climate change. Adverse effects upon ecosystem health, human health and material welfare can result from climate change. The Intergovernmental Panel on Climate Change (IPCC) developed the characterization model which is selected for the development of characterization factors. A kg carbon dioxide/kg emission is used to express the Global Warming Potential for time horizon 100 years (GWP100). This indicator has a global scale.

# 3.5.1.5 Eutrophication

This category considers the impacts of to excessive levels of macro-nutrients in the environment caused by emissions of nutrients to air, water and soil. The stoichiometric procedure of Heijungs is the base of the Nutrification potential (NP) which is expressed as kg PO4 equivalents per kg emission and the geographical scale varies between local and continental scale, time span is

infinity, and fate and exposure are not included.

# 3.5.2 Eco-Indicator 99 Method

The Eco-indicator method indicates the environmental impact in terms of numbers or scores. It simplifies the interpretation of relatively complex LCA as explained below:

1. This method includes a weighting method in LCA. After weighting it enables to give single score for each of the product or processes is calculated based on the relative environmental impact. This figure is called as Eco-Indicator. This score is represented on a point scale (Pt), where a point (Pt) represents the annual environmental load (i.e. whole production/consumption undertakings in the economy) of an average citizen (Eco-Indicator 99 (E) use load of average European) [52,53].

2. Data is collected for all basic processes and materials in advance. The eco-indicator is calculated from this. The processes and materials are defined in such a way that it fits as building blocks. For example for the production of a kilo of polythene there is a numerical value called Eco-indicator. Therefore the Eco-Indicator is a numerical value or a score that is obtained, from the LCA of a product or processes, based on the LCI. The higher value of indicates the severity of environmental impact.

The Eco-indicator 99 defines the "environment damage" in three broad categories:

# 3.5.2.1 Human Health

It includes the number and duration of diseases and loss of life years due to permanent deaths caused by environmental degradation. The effects are included mainly by: climate change, ozone layer depletion, carcinogenic effects, respiratory effects and ionization.

# 3.5.2.2. Ecosystem Quality

This category includes the impact of species diversity, acidification, ecotoxicity, eutrophication and land-use.

## 3.5.2.3 Resources

This is category basically tells the depletion of raw materials and energy resources. It is measured in terms of the surplus energy required in future for the extraction of lower quality of energy and minerals. The agricultural resource depletion is studied under the category of land use.

## 3.6. Life cycle assessment analysis of various ammonia production methods

Here are the assumptions made for the study:

- The ammonia synthesis is an exothermic process and the input energy for it is negligible.
- The inputs for nitrogen production is defined in SimaPro 7 and its values are directly used from there.
- The inputs used for SimaPro 7 calculations are feedstock, energy or electricity and emissions.

- The processes defined here for ammonia production basically involves production of hydrogen and nitrogen separately.
- The mass balance is used to identify the amount of hydrogen and nitrogen required for one kg of ammonia production.
- The fugitive emissions are considered negligible.
- CML 2001 method is used for LCA analysis.



Fig.33 Life cycle boundaries of the system for Haber Bosch process

## 3.8 Results and discussion

The impact categories considered for the CML 2001 method are: 1. Abiotic Depletion 2. Acidification 3. Eutrophication 4. Global Warming 5. Human Toxicity 6. Freshwater Aquatic Eco toxicity. The impact categories considered for Eco-indicator 99 method are: 1. Carcinogens 2. Climate Change 3. Eco toxicity 4. Acidification/Eutrophication 5. Minerals 6. Fossil fuels. These results are corresponding to one kg of Ammonia produced.



Fig.34. Global warming potential values for various ammonia production methods

The global warming potential is highest for the coal gasification method without carbon capture, followed by steam methane reforming method. The values are 3.85 kg CO<sub>2</sub>-eq and 3.03 kg CO<sub>2</sub>-eq per kg of Ammonia produced respectively. The biomass gasification has least global warming potential of 0.378 kg per kg of Ammonia produced.



Fig.35. Acidification values for various ammonia production methods



Fig.36. Eutrophication values for various ammonia production methods

The ecosystem balance essentially depends upon the nitrogen and phosphorous. The water and soil enrichment due to human activities cause undesirable impact on species. The eutrophication occurs due to emission of NOx and usage of phosphorous. The eutrophication potential of pv based methods is highest and the other methods has nearly same values.



Fig.37. Human toxicity values for various ammonia production methods



Fig.38. Freshwater aquatic eco toxicity values for various ammonia production methods



Fig.39. Carcinogens values for various ammonia production methods

The carcinogens originated from the PV based ammonia production is highest and due the fact that the materials used in manufacturing and cleaning of photovoltaic cells and the materials used in batteries are extremely hazardous for human health. The fact that the wind based methods, produce second highest carcinogens, produce approximately six times less than PV based methods makes the case of PV very significant.



Fig.40. Climate change values for various ammonia production methods

The impact on human health due to climate change is maximum for the ammonia production from coal without carbon capture and storage. It is due the high volume release of greenhouse gases and other pollutants by coal based systems, the methane and PV based systems also have substantial impact on human health.



Fig.41. Ecotoxicity values for various ammonia production methods





The abiotic depletion is highest for methane based ammonia production method and followed by ammonia production from photovoltaic method. This is due to the fact that methane is primary source of energy and feed source as well, it indicates the large consumption of methane for unit mass of ammonia produced.



Fig.43. Minerals values for various ammonia production methods



Fig.44. Fossil fuels values for various ammonia production methods





The photovoltaic electrolysis emerge an area of concern due to its very high values for acidification, ecotoxicity and human toxicity. For example the values of human toxicity is 1.366 kg 1,4-DB-eq, Freshwater aquatic ecotoxicity 0.753 kg 1,4-DB eq per kg of Ammonia produced, these values are very high as compared to all the resources considered for investigation. These high values are due to a number of hazardous materials used in the manufacturing of a photovoltaic

cell and chemicals used for cleaning. These chemicals are namely hydrochloric acid, sulfuric acid, nitric acid, hydrogen fluoride, 1,1,1-trichloroethane, and acetone. The amount depends upon the type of cell used. The thin film PV cells contain more number of toxic materials than in traditional cells. The improper handling may pose serious threat to environment and human life as indicated by the results.

The Eco-indicator 99 method also considers other categories like eco-toxicity, acidification, minerals damage, to calculate the impact on damage to human health, damage to eco-system and damage to resources and at highest level these emissions are combined as a single score. The single score of ammonia from methane is highest with a value of 0.19 mpt and ammonia from PV is 0.135 mpt for one kg of ammonia production. The damage to resources contributes maximum for methane based method whereas the carcinogens, minerals extraction and energy used equally contributes for PV based methods.

## 3. Conclusions

Considering the sub-processes discretely the LCA of ammonia production methods is performed. The constituents are considered separately produced by different pathways. Based on the studies conducted so far, the following concluding remarks are stated:

- 1) LCA is an important and reliable tool to study ammonia production analysis and assessment as it covers the period from cradle to grave.
- 2) Methane reformation and underground coal gasification has highest negative impact in terms of global warming or climate change.
- 3) Current capabilities and efficiencies of Solar PV brings grave environmental impact in terms of acidification, eutrophication and human toxicity. This is due to the fact that the manufacturing PV and batteries use extremely hazardous substances, the low efficiency of cells requires a large number of cells and area used to produce electrical energy.
- 4) Ammonia production from wind energy based water electrolysis provides a credible alternative for distributed ammonia production facilities and can boost local fertilizer production capacity.
- 5) Biomass based ammonia production proves to be most environmental benign method of ammonia production.
- 6) The renewable sources with their improved efficiency can reduce the overall environmental footprint and can replace the current fossil fuel based centralized ammonia production facilities. The high cost of renewable electricity also detrimental to renewable energy based ammonia production systems.
- 7) The LCA study establish that mitigating the environmental concerns based on toxicity due to production of PV, improving efficiency, low cost will make the renewable energy systems as a credible alternative to current fossil fuels based ammonia production systems.

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## **APPENDIX 2: PROGRESS REPORT 2 (AUGUST-OCTOBER 2015)**



# Comparative assessment of NH<sub>3</sub> production and utilization in transportation systems for Ontario

Application Ref. IT05701 Funding Request Ref.FR11885 Invoice Ref. 1516-10898 Mitacs File: ON – IRDI

**Progress Report #2** 

Period: August-October 2015

Date: 05 October 2015

### Summary

In this second progress report, we report the progress made on the following items:

- Novel ammonia production methods
- Direct use of ammonia in power generation and HVAC applications
- Ammonia usage in marine vessel applications
- Ammonia utilization in rail applications
- Ammonia vehicular opportunities and ammonia utilization in transportation sector
- Ammonia usage opportunities in mining and marine sector
- Cost, sustainability, efficiency, environmental impact assessments of various methods.

The results of the present progress report fulfill the following specific project objectives:

- An extensive study on the ammonia production from various types of resources such as renewable energies (wind, solar), methane steam reforming and excess power in nuclear and/or hydro power plants.
- A detailed study on ammonia based transportation systems and ammonia based commercial products ideas.
- Identification of opportunities for green NH<sub>3</sub> production and efficient utilization of ammonia in various sectors and especially in transportation sector.
- A comparison of the ammonia fuel cycle with conventional transportation systems in terms of sustainability and economics.

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#### PART I – BACKGROUND AND LITERATURE REVIEW

#### Novel ammonia production methods

There are multiple pathways for ammonia synthesis besides mostly used Haber-Bosch process within the literature.

#### **Electrolytic ammonia synthesis**

The synthesis of ammonia from electrochemistry is based on electrolysis where electric current is supplied to a reactor consisting of a cathode, anode, and ionic conducting membrane. The chemical reactions consist of reduction on one side and oxidation on the other with an important component being the membrane which will only conduct a special kind of ion such as protons in the form of  $H^+$ , this allows the reactor to work continuously. There are many variations of types of cathodes, anodes, and membranes however the principle remains the same where two reactants and an activation potential are applied to generate a chemical reaction resulting in ammonia synthesis. These reactions have been shown to work in a wide range of pressures and temperatures making it viable when working with atmospheric conditions.

Since ammonia consists of 3 hydrogen atoms and 1 nitrogen atom, electrochemical synthesis of ammonia requires the reaction of reactants containing these chemicals separately or in mixture. For example water contains hydrogen and air contains nitrogen. Electrochemical synthesis of ammonia is possible using these material.

There are four main categories of electrolytes used for ammonia production as shown schematically in Fig. 1. These are listed as follows:

- liquid electrolytes operating near room temperature
- molten salt electrolytes operating at intermediate temperatures (300-500°C)
- composite electrolytes consisting of a traditional solid electrolyte mixed with a low melting salt (300-700°C)
- solid electrolytes with a wide operating temperature range from near room temperature up to 700-800°C depending on the type of electrolyte membrane used.

In each type of system there is a choice for different electrodes and electrolyte systems and their operating conditions.

For the electrolytic routes, required hydrogen can be sourced from natural gas like the Haber-Bosch process or electrolysis of water, or even decomposition of an organic liquid such as ethanol. When hydrogen is produced from water electrolysis utilizing a renewable energy source such as wind or solar, environmentally pollutant emissions would noticeably diminish for ammonia production [1]. Water can also be utilized as a source of hydrogen inside the electrolytic cell through its reaction in the electrochemical process. The use of water as a source of hydrogen would also be helpful in eliminating any issues of catalyst poisoning due to traces of Sulphur compounds or CO which are common impurities in hydrogen produced via steam reforming of natural gas. The process can be carried out under ambient conditions or at higher temperatures depending on the type of the electrolyte material used. For high temperature electrolytic routes of ammonia production, the use of waste heat from thermal or nuclear power plants or heat from renewable energy sources like solar would make the overall process more environmentally friendly. Ammonia production from hydrogen and nitrogen is exothermic in nature and is facilitated by high pressures and low temperatures. Thus a balance between the operating temperature, pressure and the ammonia yield needs to be proven for each electrochemical system in determining ammonia production rates.



Fig.1. Electrochemical ammonia synthesis methods (adapted from Ref. [2])

## Liquid electrolyte based systems

In this method, Lithium perchlorate (LiClO<sub>4</sub> (0.2 M)) in tetrahydrofuran as the electrolyte and ethanol (0.18 M) as the hydrogen source can be used. In the previous studies [3], a very low current efficiency of 3-5% was achieved considering that the current density was also low (2 mA cm<sup>-2</sup>). The current efficiency may improve under a different set of experimental conditions by varying the pressure and temperature values, however, under the conditions of test, breakdown of the ionic liquid electrolyte was observed indicating severe distresses about the long term capability of the process. Furthermore the solubility of Li salts has been reported to be low in many ionic liquids [3]. This technology is at early stage of development with only small size cells evaluated in the laboratory and for a limited period of time.

## Molten salt based electrolyte systems

Current studies in molten salt based electrochemical processes have made some novel developments. Using water and atmospheric air, combining them into a molten salt of NaOH-KOH with nano-Fe<sub>2</sub>O<sub>3</sub> as the catalyst to produce a 30% current efficiency was observed [4]. The systems were using an open pot system with no separator, two nickel electrodes and a nickel monel mesh as the set up for their data. Although the efficiency seems to be lower than proton conducting membranes, its materials are inexpensive and could see improvements if the reactor set up is enhanced.

In this method, the electrodes and mesh need to be continuously inspected and replaced due to corrosion in the reactor. Electrolyte salts must be tested periodically for reactivity. When including a catalyst inside the mixture such as nano-iron oxide [4], the particles must be kept in a consistent concentration throughout the salt mixture.

In order to realize this method, a number of concepts have been demonstrated on small cells in laboratory experiments of short duration as using hydrogen, methane or water as the reactants. The technology is at an early stage of development with a good current efficiency of 72% reported for hydrogen oxidation reaction and ammonia synthesis rates of about  $3.3 \times 10^{-9}$  mol cm<sup>-2</sup>s<sup>-1</sup> [5]. A capstone student project within Dr. Dincer's research group has also been successfully realized and ammonia is synthesized in the laboratory.



Fig.2. Steam based ammonia synthesis in molten salt reactor

The reactor has water and air being supplied, water being the source for the hydrogen in the ammonia and air with the nitrogen. The molten salt begins to melt at about 170°C and at 200°C is in a molten form. High temperatures in the range of 200°C-500°C must be sustained, and a corrosive resistant material should be used.



Fig. 3. H<sub>2</sub> based ammonia synthesis in molten salt reactor



Fig.4. Photoelectro-chemical assisted molten salt ammonia synthesis

Instead of supplying steam,  $H_2$  can be directly utilized and efficiency could be increased. As seen in Fig.4, produced  $H_2$  from photoelectro-chemical process is utilized in molten salt reactor as a source of  $H^+$  ions in the reaction. Produced  $NH_3$  and unreacted  $N_2$ ,  $H_2$  are sent to a heat exchanger in order to preheat unreacted gases for the reaction. Using a condenser or chiller, gaseous ammonia can be liquidized and stored.

#### Composite membrane based systems

The composite electrolytes consist of one or more different ionic conducting phases and the second or third phase is added to the parent phase to modify electrical, thermal or mechanical properties. For example, an alkali metal carbonate and an oxide such as LiAlO<sub>2</sub> or Sm<sub>2</sub>O<sub>3</sub> doped CeO<sub>2</sub> have been shown to have oxygen-ion, carbonate ion and even proton conductivity under certain conditions (e.g. in the presence of hydrogen) [6,7].

Such materials have been under investigation as potential electrolytes for intermediate temperature (400-800°C) fuel cells and are also being employed to study ammonia production rates under a range of operating conditions.

#### Solid state electrolyte

A number of different systems, based either on proton or mixed proton/oxygen-ion conducting solid electrolytes, are undergoing research and development for application in electrochemical ammonia synthesis.

The primary components of the solid-state electrochemical device are two porous electrodes anode and cathode separated by a dense solid electrolyte, which allows ion transport of either protons or oxide ions and assists as a blockade to gas diffusion [8,9]. Solid-state proton conductors (SSPC) represent a class of ionic solid electrolytes that have the ability to conduct

hydrogen ions ( $H^+$ ) [10]. However, this method suffers from some drawbacks such as high temperature requirements and formation of secondary phases [11–13].

In the electrolytic cell, two metal electrodes are placed on both sides of the proton conductor. The gaseous H<sub>2</sub> passing over the anode will be converted to H<sup>+</sup> (Eq. 1). Hydrogen in the form of protons will be transported to the cathode where the half-cell reaction (Eq. 2) will take place; hence Eq. 3 yields the overall reaction. A schematic diagram is shown in Fig.4.

$$6H \rightarrow 6H^+ + 6e^- \tag{1}$$

$$N_2 + 6H^+ + 6e^- \rightarrow 2NH_3 \tag{2}$$

(3)

(5)

 $N_2 + 3H_2 \leftrightarrow 2NH_3$ 

For solid state ammonia synthesis, using steam rather than molecular H<sub>2</sub> is also possible as shown in Fig.5. The H<sub>2</sub>O passing over the anode will be converted to H<sup>+</sup> and O<sub>2</sub> (Eq.4):

$$3H_2O \rightarrow 6H^+ + 3/2O_2 + 6e^-$$
 (4)

Then the protons will be transported through the electrolyte to the cathode where the half-cell reaction (Eq. 2) takes place. Hence the overall reaction is:

$$3H_2O \rightarrow N_2 + 2NH_3 + 3/2O_2$$

SSAS system can be coupled to photoelectro-chemical hydrogen production as illustrated in the Fig.6.



Fig.5. Steam based SSAS in a high temperature electrochemical ammonia synthesis cell



Fig.6. SSAS using photo-electrochemically generated hydrogen

## Ceramic/inorganic proton conducting solid electrolyte based systems

A typical electrolytic cell for ammonia synthesis is fabricated by depositing electrode (catalyst) coatings on both sides of the proton conducting membrane. These porous electrodes are typically screen printed or brush coated on ceramic proton conductor membranes followed by heat treatment. Water or hydrogen is fed to the anode and nitrogen to the cathode, and ammonia is produced on the cathode side of the cell. The current collection is achieved by placing metallic meshes or sheets in contact with these electrodes. Clearly the proton conducting ceramic membrane, along with cathode or ammonia synthesis catalyst, are most important components in these systems. These membranes are required to reveal substantial proton conductivity at temperatures above 400°C [2].

#### Polymer membrane based systems

There are various types of polymer ion exchange membranes available that can be used as an electrolyte in electrochemical ammonia synthesis cells. These are: perfluorosulfonic acid membranes such as Nafion from Dupont; Flemion from Asahi Glass; Aciplex from Asahi Chemical Industry; and Dow membranes from Dow Chemical. In addition there are hydrocarbon based membranes such as polyether ether ketone (PEEK) and polybenzimidazole (PBI). These membranes can be operated in the temperature range from room temperature to 120°C. Nafion membranes are the most popular proton conducting membranes being used in the chlor-alkali industry, and in the polymer electrolyte membrane (PEM) based fuel cells and electrolysis cells [2].

Despite some stability issues for polymer membranes in the presence of ammonia, there are many advantages of using these membranes due to their high proton conductivities at lower temperatures and a large amount of information available for cell construction and assembly due to their usage in fuel cells. The low temperature operation would reduce the rate of decomposition of ammonia formed and avoid several other high temperature materials related issues.

#### O<sup>2-</sup> conducting membrane materials and ammonia synthesis systems

A large number of O<sup>2-</sup> conducting ceramic electrolytes are available and have been used in oxygen sensors, solid oxide fuel cells and for high temperature steam electrolysis. These include fully and partially stabilized ZrO<sub>2</sub> with different dopant types and levels, doped CeO<sub>2</sub>, doped LaGaO<sub>3</sub> at A-and B-sites, and doped Bi<sub>2</sub>O<sub>3</sub> [14]. The O<sup>2-</sup> conductivity feature varies significantly with the type of material used. Although some of these materials retain O<sup>2-</sup> conductivity over a wide range of temperatures, oxygen partial pressures and gas compositions, others develop either electronic or even proton conductivity in the presence of water and similar to those reported for doped BaSrO<sub>3</sub> and SrCeO<sub>3</sub> by Iwahara [15, 16].

Typically, electrochemical routes, investigated so far require operation at much lower pressures than those used in the Haber-Bosch process with operating temperatures from near room temperature for liquid and polymer electrolyte systems to between 400 and 800°C for other solid electrolytic routes. The low temperature operation has the potential to decrease material and operating costs and increase life time of the electrochemical reactor provided high ammonia production rates and high current efficiency can be achieved. Yet, one significant advantage of ammonia production by high temperature electrolytic routes is that such systems can be integrated with renewable energy, thermal or nuclear power plants to provide the waste heat for high temperature operation thus reducing the overall energy input especially if water is used as the hydrogen source. In addition to natural gas being a source of hydrogen, it can also be supplied by water electrolysis [1, 17-19].

There is also solar thermochemical ammonia synthesis process. Recent studies on solar thermochemical production of ammonia also show that a net efficiency ranging from 26% to 33% can be reached by combining the ammonia synthesis cycle with hydrogen production [20].

(6)

#### Direct use of ammonia in power generation

Ammonia combustion equation yields as:

$$4\mathrm{NH}_3 + 3\mathrm{O}_2 \rightarrow 2\mathrm{N}_2 + 6\mathrm{H}_2\mathrm{O}$$

Ammonia is predicted to be a hydrogen carrier with high hydrogen content. In a research [21], a prototype combustion unit was built that enabled liquid kerosene and gaseous ammonia to be fed, and ammonia was combusted in a gas-turbine generator. This can be said to be a great step forward for ammonia in energy-use technology, and power generation using 100 % ammonia is projected. In recent years, expectations are rising for hydrogen and hydrogen carriers as a medium for storage and transport of energy in the mass introduction and use of renewable energy. Storage and transport of hydrogen is an important issue since hydrogen is a gas under normal temperature and pressure. Hydrogen carriers are mediums that convert hydrogen into chemical substances containing large amounts of hydrogen, to simplify storage and transport. Hydrogen carriers include organic hydrides that are used by absorption and desorption of hydrogen and hydrogen that is used by direct combustion. Ammonia becomes important hydrogen carrier that does not contain any carbon atoms and has a high hydrogen ratio. Therefore, it is evaluated as a power-generating fuel. Since ammonia will generate mainly water and nitrogen on combustion, replacing a part of conventional fuel with ammonia will have a large effect in reducing carbon dioxide emissions [21].

There are following alternatives for direct ammonia usage in various applications:

- Spark-ignited internal combustion engines
- Diesel ices with H<sub>2</sub> or diesel "spike"

- Combustion turbines
- Gasoline or ethanol blend ices
- Converted biogas generators
- Direct ammonia fuel cells

Ammonia has many issues, such as its difficulty to ignite compared with general fuels and its slow burning velocity. However, with increasing expectations for the use of ammonia as a hydrogen carrier, efforts were made to verify its potential as a power-generation fuel, using a gas turbine that is able to run on diverse fuels [21].

In a recent demonstration [21], a combustor with a twin-fuel system to feed both liquid and gaseous fuel has been manufactured for stable bifuel combustion of kerosene and ammonia. Using a gas-turbine power generator with a rated output of 50 kW, ammonia equivalent to approximately 30% was added to kerosene and bifuel combustion and was conducted at approximately 40% of the rated output, at 21kW, successfully generating almost the same output as mono-fuel combustion of kerosene alone. Nitrogen oxide (NO<sub>x</sub>) in the exhaust gas was suppressed to less than 10 ppm by feeding an adequate amount of ammonia gas to a normal NO<sub>x</sub> removal unit, fully meeting the environmental standards. The gas turbine was started using only kerosene, and when stable power generation of 21 kW was achieved, nitrogen-ammonia mixed gas was fed into the gas feed line to start the combustion of ammonia. The ratio of ammonia bi-fuel combustion. When power output was maintained at a certain level during operation, the feed of kerosene could be reduced by the heat of ammonia combustion. Stable power output was maintained at 21 kW under a condition where the feed of kerosene was reduced by 30% [21].

There are basically two approaches for ammonia-fueled systems which are internal combustion engines (ICE) or fuel-cells (FCs). Generally, 6 power generation methods are now considered [22]:

- direct feed of ammonia into an internal combustion engine,
- ammonia thermal cracking and feed of the products (NH<sub>3</sub>, H<sub>2</sub> and N<sub>2</sub>) all together in the ICE cylinder for combustion,
- separation of N<sub>2</sub> and H<sub>2</sub> streams simultaneously With the decomposition such that only pure H<sub>2</sub> is combusted; and the nitrogen is expanded for work production,
- direct ammonia high-temperature fuel cell systems,
- ammonia thermal cracking and separation and further using the hydrogen into high temperature fuel cells,
- ammonia electrolysis and hydrogen used in proton exchange fuel-cells With additional exploitation of ammonia's refrigeration effect

For power generation systems, for which the storage space is readily available, the energy density is not the determining factor for the fuel selection, as the cost per BTU and emission levels are typically the important parameters. With the new energy efficient methods of producing ammonia on the cost per BTU basis, ammonia produced using renewable energy sources would be competitive with the fossil based fuels. The toxicity issue is also not as critical for power generation systems since the fuel will be handled by professionals following well established handling procedures. It is important to note that as a widely used commodity, ammonia has a perfect safety record.

#### Direct use of ammonia in transportation

By law, certain cars, vans, trucks, motorhomes and buses must pass a Drive Clean test before they can be licensed to be driven on Ontario roads. The Drive Clean Guide is incorporated by reference into Ontario Regulation 361/98 (under Environmental Protection Act, R.S.O. 1990, c. E.19) and sets out the test procedures and emission standards prescribed by the Regulation. Previous research shows that NOx emissions from ammonia-fueled ICEs is about 1/4 of that from an equivalent gasoline fueled ICEs.



Fig.7. Greenhouse gas emissions by sector in Canada (adapted from Ref. [23]) In Ontario every vehicle must undergo a tail pipe emission test every other year to check compliance with emission regulations:

- Nitrogen oxide 984 ppm @ 3000 rpm
- Carbon monoxide 0.48% @ 3000 rpm and 1.0% @ 800 rpm
- Unburned hydrocarbons 86 ppm @ 3000 rpm and 200 ppm @ 800 rpm

For each year from 1998 through 2010, the vehicle sector experienced either the largest or the second-largest decrease in emissions for each of these pollutants, and total vehicle emissions decreased more than 50% in that time. Other sources such as non-road transportation (including air, rail and marine transportation) demonstrated the least reduction in smog-causing emissions, as shown in above Fig.9.

RF (risk factor) index is used to assess the fire/explosion hazard of a flammable substance. Higher RF number indicates more fire/explosion hazard.

$$RF \ number = \frac{\left[\left(\frac{U}{L}\right)^{0.5} - 1\right]Q}{M} \tag{7}$$

where Q denotes the heat of combustion in kJ/mol and M the molecular weight of the flammable gas. U and L are the upper and lower flammability limits, respectively [25].



Fig.8. Initial pass rates of Ontario drive clean program for different vehicle types between 1999-2010 (data from Ref. [24])



Fig.9. Nitrogen oxide emissions by domestic emission source between 1998–2010 (data from Ref. [24])


Fig.10. RF number values of various fuels (data from Ref.[25]) Note that RF number for ammonia is much smaller than the other fuels which emphasized the safe and non-hazardous usage of ammonia.

In a first approach, ammonia was used to power buses in Belgium in 1942 due to an extreme shortage of diesel fuel during World War II [26]. Later the US military developed interest in ammonia combustion and theoretical and experimental studies were performed [27]. Ammonia combustion was realized successfully in spark-ignition engines while its combustion in compression-ignition engines was less successful [28-30]. There has not been significant ammonia engine research until recently due to the need to explore non-carbon fuel combustion in engines [31-33] or with a combined ammonia/hydrogen mixture [34]. It is shown in a diesel engine study that a maximum of 95% of energy replacement can be achieved when vapor ammonia is introduced into the intake manifold in combination with directly injected diesel fuel [35]. Rated power outputs can be exceeded by adding high amounts of ammonia. As more diesel fuel is replaced by ammonia in the above dual fuel operation for the same power output, CO<sub>2</sub> emissions decrease monotonically. NO<sub>x</sub> emissions show a low level until energy substitution by ammonia reaches 60% due to its lower combustion temperature [36]. As more ammonia is used, NO<sub>x</sub> emissions increase due to fuel NO<sub>x</sub> emissions.

Focusing on burning ammonia in engines, several considerations are done. These include the high ignition temperature, high latent heat, low energy content, fuel-bound nitrogen, and a low boiling point. The ignition temperature of 651°C and narrow ignition limits corresponding to 16– 25% by volume in air require a very high compression ratio for pure ammonia combustion in compression-ignition engines. After all, combustion of ammonia in engines can be achieved with proper combustion strategies. Regardless of the above challenges and limited literature on ammonia combustion in engines, the renewed interest in using ammonia as an alternative engine fuel to reduce greenhouse gas emissions has led to new research [37]. Ammonia can be an appropriate fuel for spark-ignition engines due to its high resistance to auto ignition. On the other hand, it is of great interest to use ammonia in compression-ignition engines because of the prevalence of compression ignition engine-driven electricity generators. For ICE, service network is already available and ready in addition to mature manufacturing technology. It is approximated that about 17 million engines are produced annually.



Fig.11 Various ammonia utilization pathways

In 2007, a patent [38] was issued for hydrogen and ammonia fueled internal combustion engine in the name of Hydrogen Engine Center. The patent consists of methods of operating internal combustion engines on a catalyst fuel such as hydrogen and ammonia in any proportion. The preferred way to operate the engine is to start with a hydrogen rich mixture and slowly decrease the percentage of hydrogen until the minimum amount required for proper engine operation is achieved.

In 2011, another patent [39] was issued for ammonia burning internal combustion engine in the name of Toyota. The system is designed to ignite ammonia fed into a combustion chamber by an ignition device which is arranged in the combustion chamber exhaust heat is utilized to produce hydrogen from ammonia, the hydrogen produced from the ammonia is stored in a hydrogen storing alloy.

In the patent by Dincer and Zamfirescu [40], a novel system using an ammonia decomposition and separation unit to produce pure hydrogen that is used to drive an internal combustion engine adapted to  $H_2$  as fuel; a hybrid system using a linear generator with homogeneous charge compression ignition (HCCI); and a direct ammonia high temperature fuelcell system with refrigeration for air-conditioning as a by-product are integrated to drive a vehicle. The system uses ammonia as fuel and working fluid for refrigeration and power production.

In conventional ICE, ammonia shall be dual fed together with a combustion promoter. In fact, ammonia combustion is characterized by low flame temperature, low laminar burning

velocity, high ignition energy and narrow flammability limits which would strongly hinder satisfactory engine performance. Numerous works demonstrated that hydrogen is a suitable combustion promoter [41-43]. In particular, small amount of hydrogen added to air-ammonia mixture were found to be effective to rapid combustion up allowing reasonable engine running [44]. It is remarkable that hydrogen can be obtained directly from ammonia by cracking with the aid of a solid catalyst [45, 46]. Thus, for vehicular applications hydrogen could be synthesized on board and directly injected into the ICE together with ammonia. This will prevent using expensive and space consuming hydrogen tanks. Besides, two further advantages make on board ammonia cracking very appropriate for vehicular applications. Ammonia cracking is an endothermic reaction requiring a heat source capable of maintaining the catalyst at the proper cracking temperature and thus delivering the required reaction enthalpy. Well-matched gas temperature and power in vehicular application could be available by utilizing the combusted gases exhausted by the engine, resulting in a strong increase of overall efficiency. Ammonia cracking is an equilibrium reaction [47].

Many metals, alloys and compounds of noble metals have been tested for ammonia cracking for example Fe, Ni, Pt, Ru, Ir, Pd, Rh, NiePt, Fe-MeOx and many reports can be found in the literature [48-53]. Studies devoted to the identification of the most suitable support for the active phase dispersion are available as well [47]. All in all, conversion and TOFs of metal supported on carbon or alumina was found to decrease in the order Ru > Rh > Ni > Pt > Pd > Fe [54]. Nowadays, consideration has been paid to the use of metal nitrides and carbides as well as alloys as active components for this decomposition reaction [55]. Nevertheless, although some metal nitrides and carbides have similar qualitative properties as those of noble metals, they were found to be much less suitable for ammonia decomposition, since small amounts of  $O_2$  or  $H_2O$  were found to be responsible for fast catalyst deactivation [56].



3500 rpm - low load 3000 rpm - low load 2500 rpm - low load

Fig.12. Ammonia consumption rates of specified SI engine under given conditions (data from Ref. [57])

In a study [58], combustion and emission characteristics of a compression-ignition engine that burns mixtures of ammonia and dimethyl ether (DME) were investigated. The study proposed to reduce exhaust ammonia emissions by using the direct liquid injection strategy to confine combustion inside the cylinder bowl. DME, with a high cetane number, is chosen to mix with ammonia. Because ammonia itself is not able to auto ignite due to its high resistance to auto ignition. DME also has high vapor pressure and needs to be pressurized to remain as a liquid, similar to ammonia. DME and ammonia are miscible and the mixture can remain stable due to their polarities which makes it more convenient. DME is in fact a good diesel engine fuel with low fossil fuels. Definite mixtures of ammonia/DME are available as refrigerants, thus increasing the feasibility of its use as an alternative fuel.



Fig.13. Power-engine speed curves based on various fuel mixtures (modified from Ref.[58])

It is observed that the operating range of the engine is reduced when ammonia is used. Possible reasons are as follows: Ammonia has high latent heat of 18.6 MJ/kg but low lower heating value compared diesel fuel of 42 MJ/kg. In order to provide the same fuel energy to achieve the same engine load, more ammonia is needed, approximately 2.26 times the mass of diesel fuel. This amount of ammonia, along with its higher latent heat, can cool down the in-cylinder air by nearly 100°C, assuming an equivalence ratio of 0.5 in diesel engine operation. This cooling will decelerate chemical reactions [58].

F	40% Ammonia/ 60% diesel	40% Ammonia/ 60% DME	Ammonia	Diesel fuel
LHV (MJ/kg)	32.6	24.5	18.6	42
Fuel rate (kg/ kW h)	0.316	0.42	0.554	0.245
Fuel price (\$/kg)	\$0.95	\$0.70	\$0.61	\$1.18
Fuel energy cost (\$/kWh)	\$0.30	\$0.30	\$0.34	\$0.29

Table.1 Fuel costs comparison supplied to compression ignition engine (data from Ref. [58])



Fig.14. Comparison of fuel rates and costs supplied to engine (data from Ref. [58])

The prices were taken based on \$3.7/gallon for diesel fuel, \$550/ton for ammonia, \$700/ton for DME.

In dual fueling of ammonia and diesel fuel, first step is introducing gaseous ammonia to the intake manifold by creating premixed ammonia and air mixture in the cylinder. After that diesel /biodiesel is injected to initiate combustion. In this way, there is no modifications to existing diesel injection system. Ammonia combustion efficiency can reach to 95% [59].

The results of a study [59] show that when ammonia is mixed with diesel and used as a fuel, required power stabilizes much earlier and NO emission drops quasi linearly after a while as shown in following Figs.15 and 16.



Fig.15. Constant peak torque power vs. load (modified from Ref. [59])



Fig.16. Constant peak torque NO emission in ppm (modified from Ref.[59])

## Ammonia in marine vessel applications

In marine applications, the most commonly encountered type is diesel power plant. It is utilized nearly at 90% of ships. In addition to high power, it has relatively small dimensions which is very important in the sea. Other plants (gas and steam turbine or nuclear plant) also have their own strong points and are used at various ships. Altogether, selection of optimum ship power plant depends on type, dimensions, proposed characteristics and conditions of operation of a vessel. Diesel engine is the most common type of the modern main marine engines owing to its economical operation, relatively small size and power. Since ammonia can be used as fuel for diesel generators either as duel fuel or alone, it will enable a potential source for marine applications.

Ocean Thermal Energy Conversion (OTEC) is a process that can produce electricity by using the temperature difference between deep cold ocean water and warm tropical surface waters. OTEC plants pump huge amounts of deep cold seawater and surface seawater to run a power cycle and produce electricity. OTEC is a clean energy source, environmentally sustainable and capable of providing massive levels of energy. Unlike other renewable energies, the maximum available energy from OTEC is not limited by land, shorelines, water, environmental impact, human impact and it is not intermittent. Base on the possible areas in the world, OTEC plants can be built that will be economically attractive to Hawaii, Puerto Rico and Guam. As an example, a demonstration plant on the Big Island in Hawaii is connected to the grid and generates enough electricity to power 120 homes. It is estimated that a 100-megawatt ocean thermal project could sell electricity at 20 cents per kWh [60].

Production of ammonia at the OTEC plant will basically require only hydrogen from sea water and nitrogen from air. OTEC plant ship from nitrogen extracted from the air and hydrogen obtained by electrolysis of desalinated seawater. Ammonia is formed in an equilibrium process with small evolution of heat, so that it efficiently transforms electrical energy into storable chemical energy.



Fig.17. OTEC based ammonia production plant

An example of OTEC ammonia production plant is illustrated in the Fig 17. It was proposed by Avery et al. [61] in 1980. Warm seawater is drawn from a sump, with submersible pumps, into the evaporator. The evaporator is designed to withstand extended exposure to seawater and ammonia. Pressurized liquid ammonia is fed into the evaporator through a system of pumps and valves. The evaporator includes a preheater to provide liquid ammonia to the boiler at the saturation temperature. Energy transferred from the warm seawater evaporates the ammonia and the vapor that is produced rises up through a low pressure drop mist eliminator. The mist eliminator is included in the flow path of the wet vapor to separate the liquid ammonia and to ensure minimal carryover of entrained liquid ammonia into the turbine. The separated liquid ammonia flows by gravity to the recirculation pump. The ammonia vapor exiting the evaporator flows past a series of stop and control valves before expanding through a single flow axial turbine coupled to a synchronous electrical generator. A short diffuser downstream of the turbine stage is employed to recuperate some kinetic energy. The exiting vapor passes down into a second heat exchanger condenser where it is condensed using cold seawater brought up from a depth of 1,000 m.

Several submersible pumps are used to draw the cold water from a sump connected to the cold water pump. The pressure of the ammonia condensate is increased and the liquid is transferred to the evaporator by means of a feed pump before beginning the cycle again. The ammonia power system flow loop is connected to an onsite ammonia storage and purification system. The purification system removes any water or solids which may have entered the working fluid [61].

#### Ammonia storage

Ammonia can be stored two different ways, pressurized or at low-temperature [62]. Pressurized storage keeps ammonia in liquid phase having a pressure above 8.6 bars at ambient temperature

(20°C), but ammonia is usually stored at 17 bar to keep ammonia in liquid phase if ambient temperature increases. Energy density of the liquid ammonia stored pressurized is 13.77 MJ/L. A rule of thumb is that 2.8 ton of ammonia can be stored per ton steel. This storage does not require energy to maintain the pressurized state. Low temperature storage is usually used for large-scale storage.



Fig.18. Estimated OEM costs of on board ammonia storage tanks for one personal vehicle with 482 km range (data from Ref.[63])

This type of storage requires energy to maintain its low temperature and thereby avoid boiloff due to ambient temperature. Lower capital cost is the reason why low temperature is preferred for extensive storage. Energy density of the liquid ammonia stored in this way is 15.37 MJ/L compared to 13.77 for pressurized storage. If storage time is assumed 182 days representing a period between winter and summer, will give a storage cost of 4.03 \$/GJ for ammonia. It can be mentioned that this cost is much lower compared to hydrogen storage that costs 98.74 \$/GJ.

As illustrated in Fig 18, the estimated cost of a storage tank on a personal vehicle is lowest for ammonia after standard and conventional gasoline/diesel tanks for a 300 mile range.



Fig.19. Comparison of hydrogen density and LHV values of various fuels

## Direct use of ammonia in HVAC applications

For a refrigerant to be considered a long-term option, it is advised to meet three criteria:

- Safe,
- Environmentally friendly,
- Excellent thermodynamic performance.

Several non-halogen substances, including ammonia, carbon dioxide and hydrocarbons, will work as refrigerants. All of these substances can be refrigerants for the right application if the system can be designed to meet the key selection criteria. Component and equipment manufacturers continue to research how these refrigerants perform in systems. Ammonia (NH<sub>3</sub>) has always been a dominant refrigerant in the industrial sector due to its excellent thermal properties, zero-ozone depletion potential and a global warming potential (GWP) of zero. It is classified as a B2 refrigerant by ASHRAE 34-2013 (Designation and Safety Classification of Refrigerants) for toxicity and flammability, and therefore governed by strict regulations and codes.

Ammonia is used as refrigerant prominently in the refrigeration systems of food industry like dairies, ice creams plants, frozen food production plants, cold storage warehouses, processors of fish, poultry and meat and number of other applications. Ammonia has the highest refrigerating effect per pound compared to all the refrigerants being used including the halocarbons. Although the specific volume of ammonia is high, the compressor displacement required per ton of refrigeration is quite small, due to this small compressor is required per ton of the refrigeration capacity. This saves lots of power in the long run.

For the typical conditions about -15°C in the evaporator, the condenser and the evaporator pressures are 2.37 bar and 11.67 bar respectively, which are quite moderate. Since the pressures are not very high, lightweight materials can be used for the construction of the equipment. The pressure in the evaporator is quite high so it is not necessary to expand the gas to very low pressure. This also enables high suction pressure for the compressor and lower compression ratio. The discharge temperature of the ammonia refrigerant from the compressor is high, hence water cooling of the cylinder heads and the cylinders of the compressor is very important. If high discharge pressure is required, it is advisable to use the multi-cylinder compressors instead of the single cylinder compressor to avoid overheating of the compressor.

Ammonia is available almost everywhere and is the cheapest of all the commonly used refrigerants. The remarkable differences favoring the choice of ammonia over R-134a are going to be lower overall operating costs of ammonia systems, the flexibility in meeting complex and multiple refrigeration needs, and for many applications, lower initial costs [64].

Ammonia has better heat transfer properties than most of chemical refrigerants and consequently allow for the use of equipment with a smaller heat transfer area. Thereby plant construction cost will be lower. But as these properties also benefit the thermodynamic efficiency in the system, it also reduces the operating costs of the system. In many countries the cost of ammonia per mass is considerably lower than the cost of HFCs. This advantage is even multiplied by the fact that ammonia has a lower density in liquid phase.

Modern ammonia systems are fully contained closed-loop systems with fully integrated controls, which regulate pressures throughout the system. Additionally, every refrigeration system is required by codes, which are effective, mature, and constantly updated and revised, to have safety relief valves to protect the system and its pressure vessels from over-pressurization and possible failure.

Recently, a new ammonia chilled water system was designed. It is considered as new since it has no compressor. Instead it uses the chemical properties of ammonia and heat from natural gas to condense the refrigerant which is ammonia. Originally, a chiller delivers chilled water to a chilled water loop. Cold water is circulated through a loop where it is direct into a coil in an air handler. Air is blown across a coil where a heat exchange process takes place. The air handler discharges cool conditioned air throughout a duct system. Chilled water systems are typically used in commercial air conditioning applications but there are some chilled water systems in residential applications [65].

A basic schematic of HVAC systems is illustrated in Fig.20. Ammonia can be used as a refrigerant in the cycle of HVAC systems. Additionally, for stand-alone applications, power required for compressor of HVAC system, can be produced by ammonia based power generation units so called ammonia generators as shown in Fig.20.



Fig.20. Ammonia based HVAC system schematic

As seen in Fig.20, the compressor sucks the dry gas (from evaporator and flash gas) from the separator at evaporating temperature, compresses it to condensing temperature and feeds the superheated discharge gas to the condenser. The condenser liquefies the refrigerant while dissipating the heat from the refrigerant gas to the cooling media. From the condenser, the liquid refrigerant is fed to the expansion device at condensing pressure and close to the condensing temperature. In the expansion device, the ammonia is expanded to evaporating temperature and then fed to the separator. In the separator, liquid and flash gases are separated. The liquid refrigerant, at evaporating temperature and pressure, is sucked by the pump and delivered to the evaporator. In the evaporator, the heat exchange takes place. A mix of gas and liquid is fed back to the separator, where the liquid is separated from the gas and the compressor can suck dry gas.



Fig.21. Environmental impact of chosen refrigerants and typical COP values (modified from Ref. [66])

As seen in Fig.21, ammonia based systems have higher COP values than many other refrigerants. Looking into global warming potential and ozone depletion potential, ammonia arises as the best option among all.

## Ammonia usage in mining applications

As mines become deeper, the problems of heat in the workplace become more acute. For the mining industry the energy used to keep underground temperatures at tolerable levels is a key consideration.

In mining sector, one of the biggest challenges is to provide a safe and cool enough environment for miners to work in. As a remarkable example, at the Mpong mine in South Africa, one of the richest and deepest gold mines in the world, which reaches an average depth of 2.8 km to 3.4 km below surface, an innovative hard ice plant using plate ice makers and ammonia refrigeration screw compressor sets provides essential cooling. The refrigeration plant consists of six cell ammonia evaporative condensers. It is stated that in very deep or hot mines where the temperature can exceed 50°C, ice or chilled water cooling from the surface would not reduce the ambient temperature to a safe level, which means that a further cooling system would need to be installed underground to re-chill the water or ice coming from the surface [67]. For this reason ice is made by the ammonia refrigeration plant and sent down the mine into a dam. The cold melt water is then circulated through air coolers. This is a much more energy efficient solution than a conventional chilled water refrigeration system because the latent heat capacity of a kilogram of ice means it can take up far more heat than a kilogram of cold water. The system offers significant savings in operational costs. Compared to a conventional water chiller plant, the hard ice systems offer savings of 6,788 kW per year in pumping power consumption. Compared to vacuum ice plants, the hard ice system offers savings of 581 kW per year in pumping power consumption [67].

The petroleum industry utilizes ammonia in neutralizing the acid constituents of crude oil and for protection of equipment from corrosion. Ammonia is used in the mining industry for extraction of metals such as copper, nickel, zinc and molybdenum from their ores. Ammonia is also used in nitriding (bright annealing) steel.

The diesel engine is not inherently well-suited to underground operation. The constituents of diesel exhaust are known to be carcinogenic, and underground diesel operations require extensive ventilation. Noise is too much. Proposed regulations require filtration of the exhaust to eliminate 95% of particulate matter. A result of compensating for the diesel's inherently poor health and safety characteristics is that complexity and cost will continue to rise and availability will fall. Hydride fuel cell systems obviate the complexity of underground diesel engines [68].

Tunneling and mining offer the most immediate markets for successful fuel cell vehicle commercialization. The proton-exchange membrane (PEM) fuel cell type, coupled with hydride storage, provides additional benefits critical to heavy-duty, underground applications: safety, compactness, simplicity and ruggedness [68]. Additionally, direct ammonia fuel cells could also be a practical solution for mining and tunneling applications.

## **Environmental effect of ammonia production**

Estimates were generally based on the quantity of energy consumed and the appropriate emission factors for the respective fossil fuel inputs. Natural gas was the primary fossil fuel for all estimates given in Table. Variation can be attributed to the overall efficiency of each plant which is related to plant age and design, the use of alternative fossil fuel inputs for example coal and/or oil and, to a lesser extent, the way steam exports were interpreted [69].

Country	g CO <sub>2</sub> (per kg ammonia)
Norway	1500
Netherlands	2163
Europe	1711.3
Europe average	1910
Europe modern	1660
West Europe	1550-1300
Canada	1600
USA (Ammonia plant)	1260
USA	1223
Australia (integrated ammonia/urea plant)	1250-1800

Table 2. Greenhouse gas emission factors for ammonia production (data from Refs. [69, 70])

) <u> 8</u>		
	ton CO2 eq/ton NH3 (avg)	MJ/ton NH <sub>3</sub> (avg)
Western Europe	2.34	41.6
North America	2.55	45.5
Russia&Central Europe	3.31	58.9
Chine&India	5.21	64.3
Rest of the World	2.45	43.7
World Average	3.45	52.8

Table 3. The greenhouse gas emissions and energy use from cradle (production or mining fossil fuel) to gate of ammonia production in different global regions (data from Ref. [70])

It is clear that including the additional emissions for production and transport of fossil fuels results in a significant increase of the impact of ammonia produced. For Western Europe the 20% additional greenhouse gasses per MJ natural gas used increases the greenhouse gas impact of ammonia with also 20%. Besides that a distinction in global regions using different fossil fuel mixes and different ammonia production efficiencies results in a more specific insight in impacts per ton ammonia produced [70].

## Ammonia in railway

The transportation sector was the largest contributor to GHG emissions by economic sector in Canada, corresponding about 25% of the national emission in 2012 [71]. Ammonia has significant potential as an alternative fuel to further the sustainable development of rail transportation. Rail is already a part of the NH<sub>3</sub> transport infrastructure, therefore onboard storage and transport requirements are already well understood. The vast majority of the locomotive fleet is made up of diesel-electric locomotives, operating with either two-stroke or four-stroke prime mover diesel engines that is coupled to an electric alternator/generator to convert shaft power to electric to power the traction motors and control systems. Application of NH<sub>3</sub> fuel for ICE with the alternative locomotive configurations direct feed, or a combination of direct feed and decomposition subcategory options for NH<sub>3</sub> fuel utilization in locomotives. A combination of locomotive alternatives for various type of fuels is studied in a master thesis by Hogerwaard [72].

A study for ammonia driven locomotive was conducted by Vehicle Projects LLC, which is 127-tonne fuel cell battery hybrid switcher locomotive with 250 kW of prime mover power. The locomotive's prime mover consists of two 125-kW power modules, each with complete balance of plant, for a total of 250 kW continuous net power. Because the powertrain is a parallel hybrid, the fuel cell power and traction battery power are additive. Together, they provide a peak power of at least 1.2 MW. The proposed schematic of ammonia driven locomotive is given in following Fig. [73].

Furthermore, fuel cell locomotives can help resolve the related issues of urban air quality and national energy security affecting the US rail industry and transportation sector as a whole. The issues are related by the fact that about 97% of the energy for the transport sector is based on oil, and more than 60% is imported [73].



Fig. 22. Ammonia based hydrogen production for the fuel cell locomotive (modified from Ref. [73])

## **PART II - CASE STUDIES**

Ammonia production methods based on various resources are comparatively assessed in terms of energy, exergy, sustainability, cost and life cycle considerations. All of the methods yield one kg of ammonia. Each method is illustrated in detail schematically and then simplified for cost and efficiency assessment purposes. Ammonia end product is evaluated as liquid at -34°C and 101.3 kPa.

# Methodology and Analysis

In this section, the procedures of analysis are explained.

# a) Efficiency assessment

From energy or exergy viewpoints, an indicator of how effectively the input is converted to the product is the ratio of product to input. That is, the energy efficiency  $\eta_{en}$  can be written as:

$$\eta_{en} = \frac{\text{Energy output in product}}{\text{Energy input}} = 1 - \frac{\text{Energy loss}}{\text{Energy input}}$$

and the exergy efficiency  $\eta_{ex}$  :

$$\eta_{ex} = \frac{\text{Exergy output in product}}{\text{Exergy input}} = 1 - \frac{\text{Exergy waste emission} + \text{Exergy destruction}}{\text{Exergy input}}$$

Power conversion efficiency values within this study are utilized from Refs. [74, 75].

# b) Sustainability index (SI) assessment

An important route to understand the scope for improvement or the performance of a system is through the sustainability index, which indicates how sustainable a system is in actual practice. Sustainability index supports in giving a suggestion of the improvement potential for more efficient use of the available resources of the system which is defined with the following formula [76]:

$$SI = \frac{1}{1 - \eta_{ex}}$$

Here;

 $SI = \frac{1}{D_P}$  and  $D_P = \frac{Exergy \ destruction \ rate}{Exergy \ input \ rate}$ 

DP is the depletion factor defined as the ratio of the exergy destruction rate to the input exergy rate to the system.

# c) Improvement potential (IP) assessment

The improvement potential for each of the systems can be measured in energy units based on the following relation [77]:

 $IP = (1 - \eta_{ex}) \cdot (Exergy input - Exergy output)$ 

The unit of improvement potential is kJ.

# d) Life cycle analysis

LCA is an approach from cradle to grave. This tool helps to make effective decision by analyzing the system analytically. LCA analyses the environmental impact of a product or process over the length of its entire life, beginning from raw material extraction to final disposal. LCA consider all the life stages of product or process to assess the overall environmental impact. LCA is a four-step process as in Fig.23.



Fig.23 Framework of life cycle assessment

There are a number of assessment methods evolved over the time to classify and characterize the environmental flows of system. In this study, the LCA is performed using methods CML 2001 and Eco-indicator 99.

# i. CML 2001 Method

# Depletion of Abiotic Resources

The main concern of this category is the human and ecosystem health that is affected by the extraction of minerals and fossil as inputs to the system. For each extraction of minerals and fossil fuels, the Abiotic Depletion Factor (ADF) is determined. This indicator has globe scale where it is based on concentration reserves and rate of de-accumulation.

# Human Toxicity

Toxic substances on the human environment are the main concerns for this category. In the working environment, the health risks are not included in this category. Characterization factors, Human Toxicity Potentials (HTP), are calculated with USES-LCA, describing fate, exposure and effects of toxic substances for an infinite time horizon. 1,4-dichlorobenzene equivalents/ kg emissions is used to express each toxic substance. Depending on the substance, the geographical scale varies between local and global indicator.

# Fresh Water Aquatic Eco-Toxicity

This indicator considers the impact of the emissions of toxic substances to air, water, and soil on fresh water and ecosystems. USES-LCA is used to calculate the Eco-toxicity Potential by describing fate, exposure and effects of toxic substances. 1,4-dichlorobenzene equivalents/kg emissions is used to express infinite Characterization factors which is the time horizon. The scale of this indicator can be applied to global/continental/ regional and local scale.

# Acidification potential

Acidifying substances causes a wide range of impacts on soil, groundwater, surface water, organisms, ecosystems and materials. RAINS 10 model is used to calculate the Acidification

Potential (AP) for emissions to air, describing the fate and deposition of acidifying substances. SO<sub>2</sub> equivalents/ kg emission is used to expresses the AP. This category has a different geographical scale that can be local and global. Depending on the availability the Characterization factors including fate were used. However, when not available, the factors used without fate (In the CML baseline version only factors including fate were used). The method was extended for Nitric Acid, soil, water and air; Sulphuric acid, water; Sulphur trioxide, air; Hydrogen chloride, water, soil; Hydrogen fluoride, water, soil; Phosphoric acid, water, soil; Hydrogen sulphide, soil, all not including fate. Nitric oxide, air (is nitrogen monoxide) was added including fate

# Global Warming

The greenhouse gases to air are related to the Climate change. Adverse effects upon ecosystem health, human health and material welfare can result from climate change. The Intergovernmental Panel on Climate Change (IPCC) developed the characterization model which is selected for the development of characterization factors. A kg carbon dioxide/kg emission is used to express the Global Warming Potential for time horizon 100 years (GWP100). This indicator has a global scale.

# Eutrophication

This category considers the impacts of to excessive levels of macro-nutrients in the environment caused by emissions of nutrients to air, water and soil. The stoichiometric procedure of Heijungs is the base of the Nutrification potential (NP) which is expressed as kg PO4 equivalents per kg emission and the geographical scale varies between local and continental scale, time span is infinity, and fate and exposure are not included.

# ii. Eco-Indicator 99 Method

The Eco-indicator method indicates the environmental impact in terms of numbers or scores. It simplifies the interpretation of relatively complex LCA as explained below:

- This method includes a weighting method in LCA. After weighting it enables to give single score for each of the product or processes is calculated based on the relative environmental impact. This figure is called as Eco-Indicator. This score is represented on a point scale (Pt), where a point (Pt) represents the annual environmental load (i.e. whole production/consumption undertakings in the economy) of an average citizen (Eco-Indicator 99 (E) use load of average European).
- Data is collected for all basic processes and materials in advance. The eco-indicator is calculated from this. The processes and materials are defined in such a way that it fits as building blocks. For example for the production of a kilo of polythene there is a numerical value called Eco-indicator. Therefore the Eco-Indicator is a numerical value or a score that is obtained, from the LCA of a product or processes, based on the LCI. The higher value of indicates the severity of environmental impact.

The Eco-indicator 99 defines the "environment damage" in three broad categories:

*Human Health:* It includes the number and duration of diseases and loss of life years due to permanent deaths caused by environmental degradation. The effects are included mainly by: climate change, ozone layer depletion, carcinogenic effects, respiratory effects and ionization.

*Ecosystem Quality:* This category includes the impact of species diversity, acidification, ecotoxicity, eutrophication and land-use.

*Resources:* This is category basically tells the depletion of raw materials and energy resources. It is measured in terms of the surplus energy required in future for the extraction of lower quality of energy and minerals. The agricultural resource depletion is studied under the category of land use.

Using SimaPro software for life cycle analysis, cradle to grave considerations of various ammonia production methods are investigated and comparatively assessed.

# e) Cost analysis

In the cost analysis, system advisor model (SAM) software is utilized for scenario cases. Following table prepared by US Department of Energy shows the levelized cost of electricity for various sources which is utilized for cost analysis.

		resources (	uata 11011			
Plant type	Capacity factor (%)	Levelized capital cost	Fixed O&M	Variable O&M (including fuel)	Transmission investment	Total system LCOE
Conventional Coal	85	60.4	4.2	29.4	1.2	95.1
Advanced Coal	85	76.9	6.9	30.7	1.2	115.7
Advanced Coal with CCS	85	97.3	9.8	36.1	1.2	144.4
Conventional Combined Cycle	87	14.4	1.7	57.8	1.2	75.2
Advanced Combined Cycle	87	15.9	2	53.6	1.2	72.6
Advanced CC with CCS	87	30.1	4.2	64.7	1.2	100.2
Conventional Combustion Turbine	30	40.7	2.8	94.6	3.5	141.5
Advanced Combustion Turbine	30	27.8	2.7	79.6	3.5	113.5
Advanced Nuclear	90	70.1	11.8	12.2	1.1	95.2
Geothermal	92	34.1	12.3	0	1.4	47.8
Biomass	83	47.1	14.5	37.6	1.2	100.5
Wind	36	57.7	12.8	0	3.1	73.6
Wind Offshore	38	168.6	22.5	0	5.8	196.9
Solar PV	25	109.8	11.4	0	4.1	125.3
Solar Thermal	20	191.6	42.1	0	6	239.7
Hydroelectric	54	70.7	3.9	7	2	83.5

Table 4. Estimated U.S. average levelized cost of electricity (LCOE) \$/MWh for new generation resources (data from Ref. [78])

Haber-Bosch and Electrolysis based ammonia production method requires 11-12 kWh/kg ammonia electricity in average. Therefore, cost calculations are based on electricity prices per source.

various companies				
Company Capacity (MW) Electricity Consumption (kWh/kg				
Company 1	1.5	12.5		
Company 2	6	12.5		
Company 3	7.4	11.8		
Company 4	4.7	8.3		

 Table 5. Comparison of electricity consumption for Haber-Bosch ammonia production from

Table 6. Comparison of electricity consumption for Haber-Bosch ammonia production based on type of technology

Energy Consumption (GJ/tonne)	Electricity consumption (kWh/kg)
60	16.7
28.7	8.0
41.4	11.5
19	5.3
	Energy Consumption (GJ/tonne)         60           28.7         41.4           19         19





## Steam methane reforming (SMR) based ammonia production (Method 1)

Most hydrogen produced today in the United States is made via steam-methane reforming, a mature production process in which high-temperature steam ( $700^{\circ}C-1,000^{\circ}C$ ) is used to produce hydrogen from a methane source, such as natural gas. In steam-methane reforming, methane reacts with steam under 3–25 bar pressure in the presence of a catalyst to produce hydrogen, carbon

monoxide, and a relatively small amount of carbon dioxide. Steam reforming is endothermic-that is, heat must be supplied to the process for the reaction to proceed.

In the steam reforming processes process steam is taken from the plant steam system, usually from an extraction turbine. The net consumption according to the stoichiometric conversion is 0.6-0.7 kg.kg<sup>-1</sup> NH<sub>3</sub>, the total supply at a S/C ratio of 3.0 will be about 1.5 kg.kg<sup>-1</sup> NH<sub>3</sub>. In partial oxidation much less steam is fed to the gasification reactor, but additional steam is needed in shift conversion (1.2 kg.kg<sup>-1</sup> NH<sub>3</sub> in total). The typical feedstock requirements for modern plants are approximately 22.1 GJ (LHV) t<sup>-1</sup> NH<sub>3</sub> [79].



Fig.25. Ammonia production via steam methane reforming

## **Efficiency assessment**

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.



Fig.26. Energy and material flows in SMR based ammonia production As illustrated in Fig. 26, the energy efficiency of SMR based ammonia production system can be defined as:

$$\eta_{en,1} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{steam} \cdot h_{steam} + m_{natural \ gas} \cdot LHV_{natural \ gas} + m_{nitrogen} \cdot h_{nitrogen} + W_{elecc}}$$

The exergy efficiency of SMR based ammonia production system can be written as:

 $m_{ammonia} \cdot ex_{ammonia}$ 

. . . . .

$$\eta_{ex,1} = \frac{1}{m_{steam} \cdot ex_{steam} + m_{natural gas} \cdot ex_{natural gas} + m_{nitrogen} \cdot ex_{nitrogen} + W_{elec}}$$

where exergy content of ammonia is the summation of physical and chemical exergy contents.

 $ex_{ammonia} = ex_{ph,ammonia} + ex_{ch,ammonia}$ 

 $ex_{natural gas} = ex_{ph,natural gas} + ex_{ch,natural gas}$ 

Here,  $ex_{ch,ammonia}$  and  $ex_{ch,natural gas}$  are the standard chemical exergy values while  $ex_{ph,ammonia}$  and  $ex_{ph,natural gas}$  are physical exergy contents the substances.  $W_{elec}$  is the required electricity for the overall system.

Considering the yield factor of about 10-15% from Haber-Bosch process and hydrogen production efficiency from steam methane reforming about 75%, the energy efficiency of SMR based ammonia production method is reasonable.

~		
	LHV of Natural Gas (kJ/kg)	47141
	LHV of Ammonia (kJ/kg)	18570
	Mass of Natural Gas (kg)	0.671
	Mass of Nitrogen (kg)	0.823
	Mass of Steam (kg)	1.68
	Mass of Ammonia (kg)	1
	Required Electricity $W_{elec}$ (kJ)	30204
	Required Electricity Welec (13)	50201

Table 7. Analysis parameters of SMR based ammonia production system

# Sustainability index (SI)

Sustainability index of steam methane reforming based ammonia production system can be defined as:

$$\mathrm{SI}_1 = \frac{1}{1 - \eta_{\mathrm{ex},1}}$$

# **Improvement potential (IP)**

Improvement potential of steam methane reforming based ammonia production system can be defined as:

$$IP_1 = (1 - \eta_{ex,1}) \cdot (Exergy input - Exergy output)$$

## Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 1 are illustrated respectively.





Fig.27 Abiotic depletion values of SMR based ammonia production method

Fig.28 Ozone layer depletion values of SMR based ammonia production method



Fig.29 Human toxicity values of SMR based ammonia production method

Energy efficiency Exergy efficiency Sustainability index Improvement Potent			
η <sub>en,1</sub> (%)	η <sub>ex,1</sub> (%)	SI <sub>1</sub>	IP <sub>1</sub> (kJ)
27	22	1.282	56,386

#### Wind electrolysis based ammonia production (Method 2)

Wind contributes more than 20% of total renewable electricity produced worldwide. This promotes distributed (onsite) generation, reduces the cost of transportation. The system considered for producing hydrogen from wind energy involves two main devices: a wind turbine that produces electricity, which in turn drives a water electrolysis unit that produces hydrogen. Wind energy is converted to mechanical work by wind turbines and then transformed by an alternator to alternating current (AC) electricity, which is transmitted to the power grid. The efficiency of wind turbines depends on location, with wind energy applications normally making sense only in areas with high wind activity.

Wind to ammonia systems produce ammonia through the use of electricity from wind turbine generators, which are usually large horizontal-axis wind turbines mounted on a tower. Wind turbines are commercially available in sizes up to about 2.5 MW of nameplate capacity for on-shore applications and even larger machines can be found in off-shore applications. The electrical output of the wind turbine is highly dependent on wind speed, resulting in a high variability in electrical energy production. The basic ammonia synthesis design is to use an electrolyser to produce hydrogen from water and an air separation unit to obtain nitrogen from air, both of which are combined in a Haber-Bosch synthesis reactor for production of ammonia.

#### **Efficiency assessment**

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.

As illustrated in Fig. 31, the energy efficiency of wind energy based ammonia production system can be defined as

$$\eta_{en,2} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{water} \cdot h_{water} + m_{nitrogen} \cdot h_{nitrogen} + \frac{W_{elec}}{\eta_{en,wind}}}$$

The exergy efficiency of wind energy based ammonia production system can be written as:



Fig.30. Ammonia production via wind energy based electrolysis



Fig.31. Energy and material flows in wind energy based ammonia production

/.	marybis parameters of while energy based animonia	510ddet101
	LHV of Ammonia (kJ/kg)	18570
	Mass of Nitrogen (kg)	0.823
	Mass of Water (kg)	1.59
	Mass of Ammonia (kg)	1
	Required Electricity $W_{elec}$ (kWh)	11
	Wind to Electricity Energy Efficiency $\eta_{en,\text{wind}}$ (%)	40
	Wind to Electricity Exergy Efficiency $\eta_{ex.wind}$ (%)	35

Table 9. Analysis parameters of wind energy based ammonia production system

## Sustainability analysis (SI)

Sustainability index of wind energy based ammonia production system can be defined as:

$$\mathrm{SI}_2 = \frac{1}{1 - \eta_{\mathrm{ex},2}}$$

## **Improvement potential (IP)**

Improvement potential of wind energy based ammonia production system can be defined as:  $IP_2 = (1 - \eta_{ex,2}) \cdot (Exergy \text{ input} - Exergy \text{ output})$ 

## Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 2 are illustrated respectively.







Fig.33 Ozone layer depletion values of wind electrolysis based ammonia production method





# **Cost analysis**

A scenario for wind energy based ammonia production is proposed as follows: Table 10 Parameters of wind energy scenario

Table 10. Parameters of wind energy scenario			
Metric	Value		
Location	Northeastern US		
Wind turbine	Vestas V900-1.8		
Turbine power	1800 kW		
Installed Power	57.6 kW		
Annual energy	175,112,464 kWh		
Capacity factor	34.70%		
Levelized PPA price (nominal)	6.08 ¢/kWh		
Levelized COE (nominal)	5.55 ¢/kWh		
Net present value	\$9,830,242		
Internal rate of return (IRR)	11.00%		
Year IRR is achieved	20		
IRR at end of analysis period	12.01%		
Net capital cost	\$100,966,808		

Table 11. Ammonia production cost results according to wind energy scenario

Metric	Value
Required electricity (kWh/kg)	11
Cost of electricity (¢/kWh)	5.55
Ammonia cost (¢/kg)	61.05

Table 12. Results of method 2				
Energy efficiency η <sub>en,2</sub> (%)	Exergy efficiency η <sub>ex,2</sub> (%)	Sustainability index SI <sub>2</sub>	Improvement Potential IP <sub>2</sub> (kJ)	
18.6	18	1.22	15,717	

### Solar electrolysis based ammonia production (Method 3)

Solar power is probably, along with wind power, the most readily available solution to clean energy alternatives. Solar cells produce direct current electricity from light, which can be used to power or to recharge a battery. Canada hosted the world's largest photovoltaic power plant in 2010. Sarnia Photovoltaic Power Plant in Ontario puts out 80 MW enough energy to power over 12,000 homes.



Fig.35. Ammonia production via solar energy based electrolysis

## **Efficiency assessment**

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.

As illustrated in Fig. 36, the energy efficiency of solar energy based ammonia production system can be defined as:

$$\eta_{en,3} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{water} \cdot h_{water} + m_{nitrogen} \cdot h_{nitrogen} + \frac{W_{elec}}{\eta_{en,solar}}$$

The exergy efficiency of solar energy based ammonia production system can be written as:

$$\eta_{ex,3} = \frac{m_{ammonia} \cdot ex_{ammonia}}{m_{water} \cdot ex_{water} + m_{nitrogen} \cdot ex_{nitrogen} + \frac{W_{elec}}{\eta_{ex,solar}}}$$



Fig.36. Energy and material flows in solar energy based ammonia production

T 11 12	A 1 ·	4	C 1		1 1	•	1	
I able 1 4	Analysis	narameters o	t solar	enerov	hased	ammonia	nroduction	system
1 4010 15.	1 mai y 515	parameters o	1 Solui	Unorgy	ouseu	ammonna	production	System
	<b>,</b>	1		0,			1	2

LHV of Ammonia (kJ/kg)	18570
Mass of Nitrogen (kg)	0.823
Mass of Water (kg)	1.59
Mass of Ammonia (kg)	1
Required Electricity $W_{elec}$ (kWh)	11
Solar to Electricity Energy Efficiency $\eta_{en,solar}$ (%)	20
Solar to Electricity Exergy Efficiency $\eta_{ex,solar}$ (%)	15

# Sustainability analysis (SI)

Sustainability index of solar energy based ammonia production system can be defined as:

$$\mathrm{SI}_3 = \frac{1}{1 - \eta_{\mathrm{ex},3}}$$

# **Improvement potential (IP)**

Improvement potential of solar energy based ammonia production system can be defined as:

$$IP_3 = (1 - \eta_{ex,3}) \cdot (Exergy input - Exergy output)$$

## Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 3 are illustrated respectively.



Fig.37 Abiotic depletion values of wind electrolysis based ammonia production method



Fig.38 Ozone layer depletion values of wind electrolysis based ammonia production method



Fig.39 Human toxicity values of solar electrolysis based ammonia production method

# **Cost analysis**

Table 14. Parameters of solar	energy scenario
Metric	Value
Location	Thunder Bay,CA
Annual energy	260,974 kWh
Capacity factor	14.90%
First year kWhAC/kWDC	1,306
Levelized COE (nominal)	7.04 ¢/kWh
Levelized COE (real)	5.57 ¢/kWh
Electricity cost without system	\$826,030
Electricity cost with system	\$801,836
Net savings with system	\$24,193
Net present value	\$16,883
Net capital cost	\$508,966

A scenario for solar energy based ammonia production is proposed as follows:

Table 15. Ammonia production cost results according to solar energy scenario

Metric	Value
Required electricity (kWh/kg)	11
Cost of electricity (¢/kWh)	7.04
Ammonia cost (¢/kg)	77.44

## Table 16. Results of method 3

Energy efficiency	Exergy efficiency	Sustainability index	Improvement Potential
η <sub>en,3</sub> (%)	η <sub>ex,3</sub> (%)	SI3	IP3 (kJ)
9.4	7.7	1.084	17,695

## Underground coal gasification based ammonia production (Method 4)

There are mainly two type of coal gasification. The one is called as underground coal gasification which take place below earth level and the other one is coal gasification which takes place above earth level. The second most commonly used process for hydrogen production. With depletion of oil and gas resources the dependence on coal will increase substantially.



Fig.40. Ammonia production via UCG process

## Efficiency assessment

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.



Fig.41. Energy and material flows in UCG based ammonia production

As illustrated in Fig.41, the energy efficiency of UCG based ammonia production system can be defined as:

$$\eta_{en,4} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{steam} \cdot h_{steam} + m_{coal} \cdot LHV_{coal} + m_{nitrogen} \cdot h_{nitrogen} + m_{air} \cdot h_{air} + \frac{W_{elec}}{\eta_{en,oilfired}}}$$

The exergy efficiency of UCG based ammonia production system can be written as:

 $\eta_{ex,4} = -$ 

$$m_{steam} \cdot ex_{steam} + m_{coal} \cdot ex_{coal} + m_{nitrogen} \cdot ex_{nitrogen} + m_{air} \cdot ex_{air} + \frac{W_{elec}}{\eta_{ex,oilfired}}$$

 $m_{ammonia} \cdot LHV_{ammonia}$ 

Electricity is assumed to be taken from oil fired power plant. The values of UCG process are based on Ref. [80].

Table 17. Analysis parameters of UCG based ammonia production system					
LHV of Ammonia (kJ/kg) 18570					
LHV of Coal (Illinois 6) (kJ/kg) 25088					
Mass of Nitrogen (kg) 0.823					
Mass of Steam (kg) 1					
Mass of Air (kg) 2.6					
Mass of Coal (kg) 1.36					
Mass of Ammonia (kg) 1					
Required Electricity $W_{elec}$ (kWh) 0.89					
Oil Fired Power Plant to Electricity Energy Efficiency $\eta_{en, \text{oilfired}}$ (%)	<b>b</b> ) 38				
Oil Fired Power Plant to Electricity Exergy Efficiency $\eta_{ex,oilfired}$ (%)	5) 34				

## Sustainability index (SI)

Sustainability index of UCG based ammonia production system can be defined as:

$$\mathrm{SI}_4 = \frac{1}{1 - \eta_{\mathrm{ex},4}}$$

# **Improvement potential (IP)**

Improvement potential of UCG based ammonia production system can be defined as

 $IP_4 = (1 - \eta_{ex,4}) \cdot (Exergy input - Exergy output)$ 

# Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 4 are illustrated respectively.



Fig.42 Abiotic depletion values of UCG based ammonia production method



Fig.43 Ozone layer deplation values of UCG based ammonia production method

# Underground coal gasification with carbon capture based ammonia production (Method 5)

Underground coal gasification (UCG) is an encouraging option for the future use of un-worked coal. Instead of mining coal reserves, UCG may ultimately make unreached coal reserves accessible. UCG is one of the un-mined type of electricity generation by minimal greenhouse gas emission. It prevents environmental effects, safety risks and health risks of mining. Carbon capture and storage of carbon dioxide technology are treated as two effective technologies. Underground

gasification is a process where coal, in place, is consumed by partial combustion with air, oxygen, steam, or any combination of these to produce syngas. The syngas produced through the gasification process consists mainly of hydrogen (H2) and carbon monoxide (CO).



Fig.44 Human toxicity values of UCG based ammonia production method

Energy efficiency	Exergy efficiency	Sustainability index	Improvement Potential
η <sub>en,4</sub> (%)	η <sub>ex,4</sub> (%)	SI4	IP4 (kJ)
39.6	41.9	1.721	12,849

## **Efficiency assessment**

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.

As illustrated in Fig. 46, the energy efficiency of UCG with CCS based ammonia production system can be defined as:

$$\eta_{en,5} = \frac{m_{ammonia} \cdot LHV_{ammonia} + m_{CO_2} \cdot h_{CO_2}}{m_{steam} \cdot h_{steam} + m_{coal} \cdot LHV_{coal} + m_{nitrogen} \cdot h_{nitrogen} + m_{air} \cdot h_{air} + \frac{W_{elec}}{\eta_{en,oilfired}}}$$

The exergy efficiency of UCG with CCS based ammonia production system can be written as:

. . . . .

$$\eta_{ex,5} = \frac{m_{ammonia} \cdot LHV_{ammonia} + m_{CO_2} \cdot ex_{CO_2}}{m_{steam} \cdot ex_{steam} + m_{coal} \cdot ex_{coal} + m_{nitrogen} \cdot ex_{nitrogen} + m_{air} \cdot ex_{air} + \frac{W_{elec}}{\eta_{ex,oilfired}}}$$

Electricity is assumed to be taken from oil fired power plant. The values of UCG process are based on Ref. [80].



Fig.45. Ammonia production via UCG with CCS process



Fig.46. Energy and material flows in UCG with CCS based ammonia production

Table 19. Analysis parameters of UCG with CCS based ammonia produc	tion system
LHV of Ammonia (kJ/kg) 18570	
LHV of Coal (Illinois 6) (kJ/kg) 25088	
Mass of Nitrogen (kg) 0.823	
Mass of Steam (kg) 1	
Mass of Air (kg) 2.6	
Mass of Coal (kg) 1.36	
Mass of Ammonia (kg) 1	
Mass of CO <sub>2</sub> (kg) 2.86	
Required Electricity $W_{elec}$ (kWh) 1.43	
Oil Fired Power Plant to Electricity Energy Efficiency $\eta_{en,\text{oilfired}}$ (%)	<b>6)</b> 38
Oil Fired Power Plant to Electricity Exergy Efficiency $\eta_{ex,\text{oilfired}}$ (%)	<b>6)</b> 34

## Sustainability index (SI)

Sustainability index of UCG with CCS based ammonia production system can be defined as:

$$\mathrm{SI}_5 = \frac{1}{1 - \eta_{\mathrm{ex},5}}$$

## **Improvement potential (IP)**

Improvement potential of UCG with CCS based ammonia production system can be defined as:

 $IP_5 = (1 - \eta_{ex,5}) \cdot (Exergy input - Exergy output)$ 

# Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 5 are illustrated respectively.


Fig.47 Abiotic depletion values of UCG with CCS based ammonia production method



Fig.48 Ozone layer depletion values of UCG with CCS based ammonia production method



Fig.49 Human toxicity values of UCG with CCS based ammonia production method

Table 20. Results of method 5				
Energy efficiency η <sub>en,5</sub> (%)	Exergy efficiency η <sub>ex,5</sub> (%)	Sustainability index SI5	Improvement Potential IP5 (kJ)	
35.7	37.5	1.601	15,016	

### Biomass downdraft gasifier based ammonia production (Method 6)

The biomass gasification process provides a reliable and credible alternative and one of the fastest growing renewable technologies. As an energy source, biomass can either be used directly via combustion to produce heat, or indirectly after converting it to various forms of biofuel. Conversion of biomass to biofuel can be achieved by different methods can be categorized into: thermal, chemical, and biochemical methods.



Fig.50. Ammonia production via biomass DG

# **Efficiency assessment**

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.



Fig.51 Energy and material flows in biomass DG based ammonia production

As illustrated in Fig.51, the energy efficiency of biomass downdraft gasifier based ammonia production system can be defined as:

$$\eta_{en,6} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{steam} \cdot h_{steam} + m_{coal} \cdot LHV_{coal} + m_{nitrogen} \cdot h_{nitrogen} + m_{air} \cdot h_{air} + \frac{W_{elec}}{\eta_{en,biomass}}$$

The exergy efficiency of biomass downdraft gasifier based ammonia production system can be written as:

$$\eta_{ex,6} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{steam} \cdot ex_{steam} + m_{biomass} \cdot ex_{biomass} + m_{nitrogen} \cdot ex_{nitrogen} + \frac{W_{elec}}{\eta_{ex,biomass}}}$$

Electricity is assumed to be taken from biomass fired power plant. Gasification temperature is taken as 750°C.

Table 21.	Analysis	parameters of	biomass	downdraft	gasifier	based	ammonia	product	tion s	vstem
		P			8			r		5~~~~

LHV of Ammonia (kJ/kg) 18570	_
LHV of Biomass (kJ/kg) 24747	
Mass of Nitrogen (kg) 0.823	
Mass of Steam (kg) 3	
Mass of Biomass (kg) 2	
Mass of Ammonia (kg) 1	
Required Electricity $W_{elec}$ (kJ) 1.86	
Biomass Power Plant to Electricity Energy Efficiency $\eta_{en,biomass}$ (%)	37
Biomass Power Plant to Electricity Exergy Efficiency $\eta_{ex,biomass}$ (%)	32

#### Sustainability index (SI)

Sustainability index of biomass downdraft gasifier based ammonia production system can be defined as:

$$\mathrm{SI}_6 = \frac{1}{1 - \eta_{\mathrm{ex},6}}$$

#### **Improvement potential (IP)**

Improvement potential of biomass downdraft gasifier based ammonia production system can be defined as:

 $IP_6 = (1 - \eta_{ex,6}) \cdot (Exergy input - Exergy output)$ 

#### Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 6 are illustrated respectively.



Fig.52 Abiotic depletion values of biomass DG gasification based ammonia production method



Fig.53 Ozone layer depletion values of biomass DG gasification based ammonia production method



Fig.54 Human toxicity values of biomass DG gasification based ammonia production method

Table 22. Results of method 6				
Energy efficiency η <sub>en,6</sub> (%)	Exergy efficiency η <sub>ex,6</sub> (%)	Sustainability index SI <sub>6</sub>	Improvement Potential IP <sub>6</sub> (kJ)	
30	29.1	1.412	35,091	

#### Biomass circulating fluidized bed gasifier based ammonia production (Method 6)

Circulating Fluidized Bed Gasifier (CFBG) offers a prospective technology for biomass gasification with steam. The biomass used for electricity generation varies by region. Forest by-products, such as wood residues, are common in the United States. The main contributors of waste energy are municipal solid waste, manufacturing waste, and landfill gas.



Fig.55. Ammonia production via biomass CFBG

#### **Efficiency assessment**

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.



Fig.56. Energy and material flows in biomass CFBG based ammonia production

As illustrated in Fig. 56, the energy efficiency of biomass circulating fluidized bed gasifier based ammonia production system can be defined as:

$$\eta_{en,7} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{steam} \cdot h_{steam} + m_{coal} \cdot LHV_{coal} + m_{nitrogen} \cdot h_{nitrogen} + m_{air} \cdot h_{air} + \frac{W_{elec}}{\eta_{en,biomass}}$$

The exergy efficiency of biomass circulating fluidized bed gasifier based ammonia production system can be written as:

$$\eta_{ex,7} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{steam} \cdot ex_{steam} + m_{biomass} \cdot ex_{biomass} + m_{nitrogen} \cdot ex_{nitrogen} + \frac{W_{elec}}{\eta_{ex,biomass}}}$$

Electricity is assumed to be taken from biomass fired power plant. Gasification temperature is taken as 910°C.

Table 23. Analysis parameters of biomass circulating fluidized bed gasifier based ammonia production system

LHV of Ammonia (kJ/kg)	18570	
LHV of Biomass (kJ/kg)	24747	
Mass of Nitrogen (kg)	0.823	
Mass of Steam (kg)	1	
Mass of Biomass (kg)	1.36	
Mass of Ammonia (kg)	1	
Required Electricity $W_{elec}$ (1)	xWh) 1.43	
Biomass Power Plant to Elec	etricity Energy Efficiency $\eta_{en,\text{biomass}}$ (%)	37
Biomass Power Plant to Elec	etricity Exergy Efficiency $\eta_{ex,biomass}$ (%)	32

## Sustainability index (SI)

Sustainability index of biomass circulating fluidized bed gasifier based ammonia production system can be defined as:

$$\mathrm{SI}_7 = \frac{1}{1 - \eta_{\mathrm{ex},7}}$$

### **Improvement potential (IP)**

Improvement potential of biomass circulating fluidized bed gasifier based ammonia production system can be defined as:

 $IP_7 = (1 - \eta_{ex,7}) \cdot (Exergy input - Exergy output)$ 

# Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 7 are illustrated respectively.



Fig.57 Abiotic depletion values of biomass CFBG gasification based ammonia production method



Fig.58 Ozone layer depletion values of biomass CFBG gasification based ammonia production method



Fig.59 Human toxicity values of biomass CFBG gasification based ammonia production method

Table 24. Results of method 7				
Energy efficiency η <sub>en,7</sub> (%)	Exergy efficiency η <sub>ex,7</sub> (%)	Sustainability index SI <sub>7</sub>	Improvement Potential IP7 (kJ)	
29.4	28.8	1.405	35,853	

#### Tidal and waves electrolysis based ammonia production (Method 8)

Tidal energy is one of the oldest forms of energy used by humans. Tidal power is non-polluting, reliable and predictable. Tidal barrages, undersea tidal turbines - like wind turbines but driven by the sea - and a variety of machines harnessing undersea currents are under development. Unlike wind, tidal currents are entirely predictable.

Tidal energy can be exploited in two ways (i) by building semi-permeable barrages across estuaries with a high tidal range and (ii) by harnessing offshore tidal streams.

Tidal energy schemes are characterized by low capacity factors, usually in the range of 20-35%. The technology required to convert tidal energy into electricity is very similar to the technology used in traditional hydroelectric power plants. The first requirement is a dam or "barrage" across a tidal bay or estuary. Building dams is an expensive process. Therefore, the best tidal sites are those where a bay has a narrow opening, thus reducing the length of dam which is required. At certain points along the dam, gates and turbines are installed. When there is an adequate difference in the elevation of the water on the different sides of the barrage, the gates are opened. This "hydrostatic head" that is created, causes water to flow through the turbines, turning an electric generator to produce electricity.



Fig.60. Ammonia production via tidal/waves energy based electrolysis

## **Efficiency assessment**

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.



Fig.61. Energy and material flows in of tidal and wave energy based ammonia production

As illustrated in Fig. 61, the energy efficiency of tidal and waves energy based ammonia production system can be defined as:

$$\eta_{en,8} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{water} \cdot h_{water} + m_{nitrogen} \cdot h_{nitrogen} + \frac{W_{elec}}{\eta_{en,tidal}}}$$

The exergy efficiency of tidal and waves energy based ammonia production system can be written as:

$$\eta_{ex,8} = \frac{m_{ammonia} \cdot ex_{ammonia}}{m_{water} \cdot ex_{water} + m_{nitrogen} \cdot ex_{nitrogen} + \frac{W_{elec}}{\eta_{ex,tidal}}}$$

Table 25. Analysis	parameters of tidal and	waves energy based	l ammonia proc	luction system
2		05	1	5

LHV of Ammonia (kJ/kg)	18570
Mass of Nitrogen (kg)	0.823
Mass of Water (kg)	1.59
Mass of Ammonia (kg)	1
Required Electricity $W_{elec}$ (kWh)	11
Tidal to Electricity Energy Efficiency $\eta_{en,tidal}$ (%)	85
Tidal to Electricity Exergy Efficiency $\eta_{ex,tidal}$ (%)	80

# Sustainability index (SI)

Sustainability index of tidal and waves energy based ammonia production system can be defined as:

$$\mathrm{SI}_8 = \frac{1}{1 - \eta_{\mathrm{ex},8}}$$

# **Improvement potential (IP)**

Improvement potential of tidal and waves energy based ammonia production system can be defined as:

$$IP_8 = (1 - \eta_{ex,8}) \cdot (Exergy input - Exergy output)$$

# Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 8 are illustrated respectively.



Fig.62 Abiotic depletion values of tidal&waves electrolysis based ammonia production method



Fig.63 Ozone layer depletion values of tidal&waves electrolysis based ammonia production method



Fig.64 Human toxicity values of tidal and wave based electrolysis for ammonia production

Table 26. Results of method 8				
Energy efficiency η <sub>en.8</sub> (%)	Exergy efficiency η <sub>ex.8</sub> (%)	Sustainability index SI <sub>8</sub>	Improvement Potential IP <sub>8</sub> (kJ)	
39.5	41.3	1.702	11,266	

#### **Coal gasification based ammonia production (Method 9)**

Coal gasification is used to produce synthetic gas as the input to the Haber-Bosch process. This gasification process involves an exothermic reaction of coal with a mixture of oxygen and steam to produce synthetic gas, mainly consisting of carbon monoxide and hydrogen.

## **Efficiency assessment**

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.

As illustrated in Fig. 66, the energy efficiency of coal gasification based ammonia production system can be defined as:

$$\eta_{en,9} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{steam} \cdot h_{steam} + m_{coal} \cdot LHV_{coal} + m_{nitrogen} \cdot h_{nitrogen} + m_{air} \cdot h_{air} + \frac{W_{elec}}{\eta_{en,oilfired}}}$$

The exergy efficiency of coal gasification based ammonia production system can be written as:

$$\eta_{ex,9} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{steam} \cdot ex_{steam} + m_{coal} \cdot ex_{coal} + m_{nitrogen} \cdot ex_{nitrogen} + m_{air} \cdot ex_{air} + \frac{W_{elec}}{\eta_{ex,oilfired}}}$$

. . . . .

Electricity is assumed to be taken from oil fired power plant. The parameters are taken from Ref.[81] and the gasification temperature is considered as 1150°C.



Fig. 65. Ammonia production via coal gasification



Fig.66. Energy and material flows of coal gasification based ammonia production

		- J -
LHV of Ammonia (kJ/kg)	18570	
LHV of Coal (Illinois 6) (kJ/kg)	25088	
Mass of Nitrogen (kg)	0.823	
Mass of Steam (kg)	1	
Mass of Air (kg)	2.6	
Mass of Coal (kg)	1.36	
Mass of Ammonia (kg)	1	
Required Electricity $W_{elec}$ (kWh)	0.79	
Oil Fired Power Plant to Electricity Energy Efficiency	$\eta_{en, oilfired}$ (%)	38
Oil Fired Power Plant to Electricity Exergy Efficiency	$\eta_{ex, oilfired}$ (%)	34

Table 27. Analysis parameters of coal gasification based ammonia production system

### Sustainability index (SI)

Sustainability index of coal gasification based ammonia production system can be defined as:

$$SI_9 = \frac{1}{1 - \eta_{ex,9}}$$

# **Improvement potential (IP)**

Improvement potential of coal gasification based ammonia production system can be defined as:

 $IP_9 = (1 - \eta_{ex,9}) \cdot (Exergy \ input - Exergy \ output)$ 

# Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 9 are illustrated respectively.











Fig.69 Human toxicity values of coal gasification based ammonia production method

Table 28.	Results	of method	9
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Energy efficiency	Exergy efficiency	Sustainability index	Improvement Potential
η <sub>en,9</sub> (%)	η <sub>ex,9</sub> (%)	SI9	IP9 (kJ)
23.3	23.9	1.314	45,357

#### Geothermal electrolysis based ammonia production (Method 10)

The most active geothermal resources are usually found along major plate boundaries where earthquakes and volcanoes are concentrated. Most of the geothermal activity in the world occurs in an area called the "Ring of Fire". This area encircles the Pacific Ocean. When magma comes close to the surface, it heats ground water found trapped in porous rock or water running along fractured rock surfaces and faults. These features are called hydrothermal. They have two common ingredients: water (hydro) and heat (thermal). Drilling a well and testing the temperature deep underground is the most reliable method for finding a geothermal reservoir. Geothermal energy has the potential to play a significant role in moving the United States and Canada toward a cleaner, more sustainable energy system. It is one of the few renewable energy technologies that - like fossil fuels - can supply continuous, base load power.

Canadian companies develop geothermal electricity in the U.S., yet the resource remains largely untapped this side of the border. Canada is the only country along the Pacific Rim that doesn't have an operating, high-temperature geothermal energy power plant. Systematic investigation of geothermal resources in Canada commenced in 1973, when the worldwide oil crisis spurred countries to seek alternatives to imported oil. A formal program concluding in 1986, without leading to any major development projects. Momentum didn't pick up again until the early 2000s, when oil prices again began to rise [82].

Some areas in Western Canada display strong prospects for geothermal energy extraction, and there have been extensive studies at Mount Meager, north of Whistler, BC. Electricity was successfully produced there during testing in the past, but as of 2010, the facility was not operational [83]. Further, the site's new lease holders, Ram Power, have indicated that the site is a low priority compared to its other international projects [84].

The Ring of Fire around the Pacific region is one of the most seismically active regions in the world and every country around it has built geothermal power plants to take advantage of the geothermal resources. That is, except Canada. The Con Mine District Heating System in Yellowknife has also qualified for financial support from the Clean Energy Fund (\$14.1 million) though a lack of support from city residents in a March 2011 referendum means that locals are unwilling to borrow funds for the project. The proposed heating system would produce 52,000 MWh/yr which could be used to heat nearly 40 commercial buildings in downtown Yellowknife, offsetting ~7.5 million litres of heating oil annually [83]. A pilot project to test the viability of electricity and heat production through the use of existing oil and gas infrastructure is underway in Swan Hills, Alberta. Various direct heating projects are also in development, including a demonstration for a greenhouse in Chilliwack, BC, and a plastics factory in Springhill, Nova Scotia [83].



Fig.70. Ammonia production via geothermal energy based electrolysis

#### **Efficiency assessment**

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.

As illustrated in Fig.71, the energy efficiency of geothermal energy based ammonia production system can be defined as:

$$\eta_{en,10} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{water} \cdot h_{water} + m_{nitrogen} \cdot h_{nitrogen} + \frac{W_{elec}}{\eta_{en,geothermal}}}$$

The exergy efficiency of geothermal energy based ammonia production system can be written as:  $m_{ammonia} \cdot ex_{ammonia}$ 

$$\eta_{ex,10} = \frac{m_{ammonia} \cdot ex_{ammonia}}{m_{water} \cdot ex_{water} + m_{nitrogen} \cdot ex_{nitrogen} + \frac{W_{elec}}{\eta_{ex,geothermal}}}$$



Fig.71. Energy and material flows of geothermal energy based ammonia production

Table 29. Analysis parameters of geothermal energy based ammonia production system

LHV of Ammonia (kJ/kg)	18570
Mass of Nitrogen (kg)	0.823
Mass of Water (kg)	1.59
Mass of Ammonia (kg)	1
Required Electricity $W_{elec}$ (kWh)	11
Geothermal to Electricity Energy Efficiency $\eta_{en,geothermal}$ (%)	35.6
Geothermal to Electricity Exergy Efficiency $\eta_{ex,\text{geothermal}}$ (%)	20

# Sustainability index (SI)

Sustainability index of geothermal energy based ammonia production system can be defined as:

$$SI_{10} = \frac{1}{1 - \eta_{ex,10}}$$

### **Improvement potential (IP)**

Improvement potential of geothermal energy based ammonia production system can be defined as:

 $IP_{10} = (1 - \eta_{ex,10}) \cdot (Exergy input - Exergy output)$ 

#### Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 10 are illustrated respectively.







Fig.73 Ozone layer depletion values of geothermal energy based ammonia production method



Fig.74 Human toxicity values of geothermal energy based ammonia production method

# **Cost analysis**

Using System Advisor Model (SAM) software, geothermal cost analysis is conducted for Saskatoon region. LCOE of geothermal based electricity is calculated higher than average because of lower geothermal temperature and deeper wells.

Metric	Value
Location	Saskatoon,CA
First Year Energy	66,732,236 kWh
Capacity factor	36.50%
PPA price (Year 1)	19.48 ¢/kWh
PPA price escalation	1.00%
Levelized PPA price (nominal)	21.12 ¢/kWh
Levelized COE (nominal)	19.99 ¢/kWh
Net present value	\$6,998,542
Internal rate of return (IRR)	11.00%
Year IRR is achieved	20
IRR at end of analysis period	12.99%
Net capital cost	\$73,172,480

Table 30. Parameters for geothermal energy scenario

T 1 1 0 1 A ·	1	. 1.	1. /	.1 1	•
Table (1 Ammonia)	production (	cost results	according to	geothermal	energy scenario
	production	cost results	according to	Scotherman	onorgy seemano

	Metric		Value	
	Required elect	Required electricity (kWh/kg) 11		
	Cost of electric	Cost of electricity (¢/kWh) 19.99		
	Ammonia cost	(¢/kg)	219.89	
	Table 32. I	Results of metho	d 10	
Energy efficiency η <sub>en,10</sub> (%)	Exergy efficiency η <sub>ex,10</sub> (%)	Sustainability SI <sub>10</sub>	index	Improvement Potential IP <sub>10</sub> (kJ)
16.6	10.31	1.115		17,200

# Hydroelectric electrolysis based ammonia production (Method 11)

Canada is the world's third largest producer of hydroelectricity, generating 348.1 billion kWh in 2010 [85]. More than 70,000 MW of hydropower have been developed from a total of approximately 475 generating facilities across the country [86]. In 2010, hydropower generated 321,061,668 MWh, considerably more than conventional steam generation at 95,415,784 MWh [87]. Total utility generation emerged at 527,689,407 MWh, demonstrating hydro's 60% dominance share of Canada's electricity production. A single power plant, like the Robert-Bourassa station in northern Quebec, can meet the needs of 1.4 million people [88]. As with coal and gas, Canada has come to hydropower as a result of convenience; it has abundant supplies of rushing water, mountainous regions, and steady rainfall. Canada's surface water resources are substantial about 7% of the world's renewable water supply [89].

Contrasting all other renewable energies, hydropower has served Canada on a major scale for over a century. Large scale development began in earnest in the early 1900s, with sites constructed in at Niagara and Shawnigan. Large stations erected in the 1960s and 70s marked a settling time for expansion, with very few new hydro sites developed into the mid-90s, and almost no new sites as of 2005. Some reports state Canada has already maximized on its hydropower potential, leaving no promising sites for new development [90]. Others, including an Environment Canada study, report undeveloped potential of more than double the current capacity. Environmental and social concerns have hampered the approval of conventional storage facility plans. In conventional hydro's demise, run-of-river systems, which avoid many of the unfavorable aspects of large hydro, have gained much attention.

Canada's long history with hydropower has fostered experience and skill in both facility design and construction. Some of the world's largest and most efficient hydropower facilities involved Canadian architects, engineers and builders. Canadian development of hydropower facilities has occurred in Colombia, Ghana, Malaysia, India and the Philippines, among others. Canada is also the United States' biggest supplier of electricity, alongside oil, natural gas and uranium. In 2009, Canada's energy exports to the U.S were valued at \$76.27 billion, with nearly 2/3 of energy accounted for with hydropower [91]. In 2010, BC contributed 5,670,655 MWh of electricity to exports for the U.S., the bulk of which was generated by hydropower [92]. Proposals for submarine power cables carrying electricity from Canada to the U.S. were announced in early 2011. The plans, advanced by several different companies, would establish submarine power cables between British Columbia and California, Montreal and New York City, and potentially from Newfoundland and Manitoba to northeastern and Midwestern American markets [93].

Vancouver Island is served by three sets of submarine cables, and the technology is used in transmitting power from offshore wind farms as well. The environmental concerns of laying power cables along the ocean floor include the freighting of massive amounts of material (usually from Japan), and the disturbance of marine life during construction. Quebec accounts for the majority of hydroelectric production in Canada. The eastern province draws 94% of its power from hydroelectric facilities. With a capacity of 34,490 MW in 2010, hydropower supports over four million customers there [94]. British Columbia is the country's second largest producer, with an installed generating capacity of over 11,000 MW [95].

#### **Efficiency assessment**

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.



Fig.75. Energy and material flows of hydropower based ammonia production



Fig.76. Ammonia production via hydropower based electrolysis

As illustrated in Fig. 75, the energy efficiency of hydroelectric energy based ammonia production system can be defined as:

$$\eta_{en,11} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{water} \cdot h_{water} + m_{nitrogen} \cdot h_{nitrogen} + \frac{W_{elec}}{\eta_{en,hydro}}}$$

The exergy efficiency of hydroelectric energy based ammonia production system can be written as:  $m = 1 + e^{r}$ 

$$\eta_{ex,11} = \frac{m_{ammonia} \cdot ex_{ammonia}}{m_{water} \cdot ex_{water} + m_{nitrogen} \cdot ex_{nitrogen} + \frac{W_{elec}}{\eta_{ex,hydro}}$$

LHV of Ammonia (kJ/kg)18570Mass of Nitrogen (kg)0.823Mass of Water (kg)1.59Mass of Ammonia (kg)1Required Electricity $W_{elec}$ (kWh)11Hydroelectric to Electricity Energy Efficiency $\eta_{en,hydro}$ (%)92Hydroelectric to Electricity Exergy Efficiency $\eta_{ex,hydro}$ (%)90	ne 55.	Analysis parameters of nyuroelectric energy based anniholita	production
Mass of Nitrogen (kg)0.823Mass of Water (kg)1.59Mass of Ammonia (kg)1Required Electricity $W_{elec}$ (kWh)11Hydroelectric to Electricity Energy Efficiency $\eta_{en,hydro}$ (%)92Hydroelectric to Electricity Exergy Efficiency $\eta_{ex,hydro}$ (%)90		LHV of Ammonia (kJ/kg)	18570
Mass of Water (kg)1.59Mass of Ammonia (kg)1Required Electricity $W_{elec}$ (kWh)11Hydroelectric to Electricity Energy Efficiency $\eta_{en,hydro}$ (%)92Hydroelectric to Electricity Exergy Efficiency $\eta_{ex,hydro}$ (%)90		Mass of Nitrogen (kg)	0.823
Mass of Ammonia (kg)1Required Electricity $W_{elec}$ (kWh)11Hydroelectric to Electricity Energy Efficiency $\eta_{en,hydro}$ (%)92Hydroelectric to Electricity Exergy Efficiency $\eta_{ex,hydro}$ (%)90		Mass of Water (kg)	1.59
Required Electricity $W_{elec}$ (kWh)11Hydroelectric to Electricity Energy Efficiency $\eta_{en,hydro}$ (%)92Hydroelectric to Electricity Exergy Efficiency $\eta_{ex,hydro}$ (%)90		Mass of Ammonia (kg)	1
Hydroelectric to Electricity Energy Efficiency $\eta_{en,hydro}$ (%) 92 Hydroelectric to Electricity Exergy Efficiency $\eta_{ex,hydro}$ (%) 90		Required Electricity $W_{elec}$ (kWh)	11
Hydroelectric to Electricity Exergy Efficiency $\eta_{ex,hydro}$ (%) 90		Hydroelectric to Electricity Energy Efficiency $\eta_{en,hydro}$ (%)	92
		Hydroelectric to Electricity Exergy Efficiency $\eta_{ex,hydro}$ (%)	90

Table 33. Analysis parameters of hydroelectric energy based ammonia production system

# Sustainability index (SI)

Sustainability index of hydroelectric energy based ammonia production system can be defined as:

$$SI_{11} = \frac{1}{1 - \eta_{ex,11}}$$

# **Improvement potential (IP)**

Improvement potential of hydroelectric energy based ammonia production system can be defined as:

 $IP_{11} = (1 - \eta_{ex,11}) \cdot (Exergy input - Exergy output)$ 

# Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 11 are illustrated respectively.



Fig.77 Abiotic depletion values of hydroelectric energy based ammonia production method



Fig.78 Ozone layer depletion values of hydroelectric energy based ammonia production method



Fig.79 Human toxicity values of hydroelectric energy based ammonia production method

Table 34. Results of method 11					
Energy efficiency	Exergy efficiency	Sustainability index	<b>Improvement Potential</b>		
η <sub>en,11</sub> (%)	η <sub>ex,11</sub> (%)	$SI_{11}$	IP <sub>11</sub> (kJ)		
42.7	46.4	1.866	10,277		

# Ocean thermal electrolysis based ammonia production (Method 12)

An Ocean Thermal Energy Conversion (OTEC) is a solar based energy source utilizing the temperature difference between the ocean surface and deep ocean waters. Near the equator, solar energy warms the top 50-100 m of ocean to a temperature of 27-30°C while ocean water at a depth of 1,000 m remains at or below 5°C [96]. To extract the energy, a vapor-power cycle is constructed by using the hot and cold heat reservoirs of ocean water. Warm surface water is passed through a heat exchanger to boil a liquid with a low boiling point, such as ammonia, propane, or fluorocarbons, which is then passed through a turbine to drive an electric generator, similar to a conventional steam Rankine cycle power plant. The fluid leaving the turbine is condensed in another heat exchanger by using the cold water extracted from deep in the ocean. To repeat the

cycle, the condensed working fluid is pumped back to the first heat exchanger where the warm ocean surface water once again boils the liquid for use in the turbine.

The advantage of using OTEC is the constant availability of the renewable resource during each and every day and hour of the year, unlike other renewable energy resources, such as wind and solar, which tend to have a cyclical and unpredictable nature of energy production. One of the complications with OTEC power generation is the transportation of the energy generated to the end users. Storing the generated energy in chemical form, such as ammonia, may help solve this problem and make the technology feasible. It was suggested such a design in 1985, consisting of a 325 MW net electrical output OTEC plant producing ammonia at a rate of 1,000 t/day [96]. The plant would distill and electrolyze sea water to produce hydrogen that can then be combined with nitrogen, separated from air, to make ammonia. The ammonia would then be cooled and stored onboard the OTEC plant before being transported to land via tankers and used as either a transportation fuel or in the ammonia fertilizer industry [96].

The technology to construct a commercial power plant was verified in a test of MINI-OTEC in 1979 near Keahole Point, Hawaii. MINI-OTEC was a small, closed loop system that used ammonia as the working fluid, and in addition, was the first at sea plant to produce net power. The plant generated 50 kW of electrical energy during operation. However, it consumed 21.3 kW to power the seawater pumps, although additional losses in the system reduced the net power output to 17.3 kW [97]. The proposed 1,100 t/day, 365 MW full-scale plant would provide the motor vehicle fuel equivalent of 150,000 gal-gasoline/day. Approximately 2,000 of these plants would be needed to supply all of the energy needed by automobiles in the United States, which would result in a OTEC facility spacing of 175 km throughout the tropical ocean [98]. The MINI-OTEC plant produced little power; however it did prove the concept of using OTEC to generate a net amount of electricity. The ability of OTEC to produce a net amount of power was further supported in a paper by Avery et al. in 1999, which stated that a 46 MW pilot plant needs to be built to further test full scale feasibility [98].



Fig.80. Ammonia production via OTEC based electrolysis

## **Efficiency assessment**

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.



Fig.81. Energy and material flows of OTEC energy based ammonia production

As illustrated in Fig. 81, the energy efficiency of OTEC based ammonia production system can be defined as:

$$\eta_{en,12} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{water} \cdot h_{water} + m_{nitrogen} \cdot h_{nitrogen} + \frac{W_{elec}}{\eta_{en,otec}}}$$

The exergy efficiency of OTEC based ammonia production system can be written as:

$$\eta_{ex,12} = \frac{m_{ammonia} \cdot ex_{ammonia}}{m_{water} \cdot ex_{water} + m_{nitrogen} \cdot ex_{nitrogen} + \frac{W_{elec}}{\eta_{ex,otec}}}$$

Table 35. Analysis parameters of OTEC based ammonia production system

LHV of Ammonia (kJ/kg)	18570
Mass of Nitrogen (kg)	0.823
Mass of Water (kg)	1.59
Mass of Ammonia (kg)	1
Required Electricity W <sub>elec</sub> (kWh)	11
OTEC to Electricity Energy Efficiency $\eta_{en,\text{otec}}$ (%)	7
OTEC to Electricity Exergy Efficiency $\eta_{ex,otec}$ (%)	6

# Sustainability index (SI)

Sustainability index of OTEC based ammonia production system can be defined as:

$$SI_{12} = \frac{1}{1 - \eta_{ex,12}}$$

# **Improvement potential (IP)**

Improvement potential of OTEC based ammonia production system can be defined as:

$$IP_{12} = (1 - \eta_{ex,12}) \cdot (Exergy input - Exergy output)$$

# Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 12 are illustrated respectively.



Fig.82 Abiotic depletion values of OTEC based ammonia production method



Fig.83 Ozone layer depletion values of OTEC based ammonia production method

	Table 36. I	Results of method 12	
Energy efficiency η <sub>en,12</sub> (%)	Exergy efficiency η <sub>ex,12</sub> (%)	Sustainability index SI <sub>12</sub>	Improvement Potential IP <sub>12</sub> (kJ)
3.3	3	1.032	18,585



Fig.84 Human toxicity values of OTEC based ammonia production method

# Nuclear electrolysis based ammonia production (Method 13)

Ever since the beginning of the nuclear age, Canada has been at the forefront of nuclear power development. The country's first civilian reactor opened in 1971, and today Canada operates 18 of them: 16 in Ontario, and one each in New Brunswick and Quebec.



Fig.85 Ammonia production via nuclear based electrolysis

# **Efficiency assessment**

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.



Fig.86 Energy and material flows of nuclear electrolysis based ammonia production

As illustrated in Fig. 86, the energy efficiency of nuclear electrolysis based ammonia production system can be defined as:

$$\eta_{en,13} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{water} \cdot h_{water} + m_{nitrogen} \cdot h_{nitrogen} + \frac{W_{elec}}{\eta_{en \, \text{nucleice}}}$$

The exergy efficiency of nuclear electrolysis based ammonia production system can be written as:

$$\eta_{ex,13} = \frac{m_{ammonia} \cdot ex_{ammonia}}{m_{water} \cdot ex_{water} + m_{nitrogen} \cdot ex_{nitrogen} + \frac{W_{elec}}{\eta_{ex,nuc.elec}}}$$

Table 37. Analysis parameters of nuclear electrolysis based ammonia production system

LHV of Ammonia (kJ/kg)	18570
Mass of Nitrogen (kg)	0.823
Mass of Water (kg)	1.59
Mass of Ammonia (kg)	1
Required Electricity $W_{elec}$ (kWh)	11
Nuclear to Electricity Energy Efficiency $\eta_{en,\text{nuc.elec.}}$ (%)	35
Nuclear to Electricity Exergy Efficiency $\eta_{ex.nuc.elec.}$ (%)	30

# Sustainability index (SI)

Sustainability index of nuclear electrolysis based ammonia production system can be defined as:

$$SI_{13} = \frac{1}{1 - \eta_{ex,13}}$$

## **Improvement potential (IP)**

Improvement potential of nuclear electrolysis based ammonia production system can be defined as:

 $IP_{13} = (1 - \eta_{ex,13}) \cdot (Exergy input - Exergy output)$ 

# Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 13 are illustrated respectively.



Fig.87 Abiotic depletion values of nuclear electrolysis based ammonia production method



Fig.88 Ozone layer depletion values of nuclear electrolysis based ammonia production method



Fig.89 Human toxicity values of nuclear electrolysis based ammonia production method

Table 38. Results of method 13				
Energy efficiency	Exergy efficiency	Sustainability index	<b>Improvement Potential</b>	
η <sub>en,13</sub> (%)	η <sub>ex,13</sub> (%)	$SI_{13}$	<b>IP</b> <sub>13</sub> ( <b>kJ</b> )	
16.4	15.5	1.183	16,211	

### Partial oxidation of heavy oil based ammonia production (Method 14)

Heavy fuel oil is the residue of crude oil distillation that still flows, waste oil from other industries are often added. It is the fuel used in large marine vessels because of price (about half the price of distillates). A typical HFO is IF-300 (Intermediate Fuel), which has a viscosity of 300·10-6 m2/s at 50 °C (300 cSt), 25·10-6 m<sup>2</sup>/s at 100 °C,  $\rho$ =990 kg/m<sup>3</sup> at 15 °C, HHV=43 MJ/kg, and the flashpoint at 60-80 °C. HFO may have a composition of 88% wt C, 10 % wt H, 1 % wt S, 0.5 % wt H<sub>2</sub>O, 0.1 % wt ash, and may contain dispersed solid or semi-solid particles (asphaltenes, minerals and other leftovers from the oil source, metallic particles from the refinery equipment, and some dumped chemical wastes), plus some 0.5 % water.



Fig.90. Ammonia production via partial oxidation of heavy oil

#### **Efficiency assessment**

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.



Fig.91. Energy and material flows of partial oxidation of heavy oil based ammonia production

As illustrated in Fig. 91, the energy efficiency of partial oxidation of heavy oil based ammonia production system can be defined as:

$$\eta_{en,14} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{water} \cdot h_{water} + m_{O_2} \cdot h_{O_2} + m_{heavy oil} \cdot LHV_{heavy oil} + m_{nitrogen} \cdot h_{nitrogen} + \frac{W_{elec}}{\eta_{en,heavyoil}} + Q_{in}}$$

The exergy efficiency of partial oxidation of heavy oil based ammonia production system can be written as:

$$\eta_{en,14} = \frac{m_{ammonia} \cdot ex_{ammonia}}{m_{water} \cdot ex_{water} + m_{O_2} \cdot ex_{O_2} + m_{heavy oil} \cdot ex_{heavy oil} + m_{nitrogen} \cdot ex_{nitrogen} + \frac{W_{elec}}{\eta_{ex,heavyoil}} + Q_{in} \left(1 - \frac{T}{T_0}\right)}$$

where exergy content of ammonia and heavy oil is the summation of physical and chemical exergy contents.

 $ex_{ammonia} = ex_{ph,ammonia} + ex_{ch,ammonia}$ 

 $ex_{heavy\,oil} = ex_{ph,heavy\,oil} + ex_{ch,heavy\,oil}$ 

Here,  $ex_{ch,ammonia}$  and  $ex_{ch,heavy oil}$  are the standard chemical exergy values while  $ex_{ph,ammonia}$  and  $ex_{ph,heavy oil}$  are physical exergy contents the substances. Partial oxidation temperature is taken as 800°C.

### Sustainability index (SI)

Sustainability index of partial oxidation of heavy oil based ammonia production system can be defined as:

$$SI_{14} = \frac{1}{1 - \eta_{ex,14}}$$

### **Improvement potential (IP)**

Improvement potential of partial oxidation of heavy oil based ammonia production system can be defined as:

$$IP_{14} = (1 - \eta_{ex,14}) \cdot (Exergy input - Exergy output)$$

# Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 14 are illustrated respectively.

LHV of Heavy Oil (kJ/kg)	40000	
LHV of Ammonia (kJ/kg)	18570	
Mass of Heavy Oil (kg)	1.257	
Mass of Nitrogen (kg)	0.823	
Mass of Oxygen (kg)	0.5	
Mass of Water (kg)	1	
Mass of Ammonia (kg)	1	
Required Electricity Welec (kWh)	0.19	
Required Heat $Q_{in}$ (kWh)	0.01	
Heavy Oil to Electricity Energy Efficiency $\eta_e$	n,heavyoil (%)	35
Heavy Oil to Electricity Exergy Efficiency $\eta_e$	r heavyoil (%)	30

Table 39. Analysis parameters of partial oxidation of heavy oil based ammonia production system





Table 40. Results of method 14				
Energy efficiency	<b>Improvement Potential</b>			
η <sub>en,14</sub> (%)	$\eta_{ex,14}$ (%)	<b>SI</b> 14	<b>IP</b> <sub>14</sub> ( <b>kJ</b> )	
35	36	1.561	22,292	



Fig.93 Ozone layer depletion values of partial oxidation of heavy oil based ammonia production method



Fig.94 Human toxicity values of partial oxidation of heavy oil based ammonia production method

# Nuclear high temperature electrolysis based ammonia production (Method 15)

Canada is the world's second-largest uranium producer behind Kazakhstan. Canada also hosts some of the biggest reserves with close to 500,000 tonnes of uranium recoverable, though it is well behind Australia (1,673,000 tonnes) and Kazakhstan (651,000 tonnes). Nuclear fuel is comparatively cheap (on a per kWh basis) and relatively abundant, the plant itself is time consuming to build.



Fig.95 Ammonia production via nuclear high temperature electrolysis

# **Efficiency assessment**

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.



Fig.96 Energy and material flows of nuclear high temperature electrolysis based ammonia production

As illustrated in Fig. 96, the energy efficiency of nuclear high temperature electrolysis based ammonia production system can be defined as:

$$\eta_{en,15} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{water} \cdot h_{water} + m_{nitrogen} \cdot h_{nitrogen} + \frac{W_{elec}}{\eta_{en,nuc.ht.elec.}} + Q_{in}}$$

The exergy efficiency of nuclear high temperature electrolysis based ammonia production system can be written as:

$$\eta_{ex,15} = \frac{m_{ammonia} \cdot ex_{ammonia}}{m_{water} \cdot ex_{water} + m_{nitrogen} \cdot ex_{nitrogen} + \frac{W_{elec}}{\eta_{ex,\text{nuc.ht.elec.}}} + Q_{in} \left(1 - \frac{T}{T_0}\right)$$

Here, temperature T is taken as  $750^{\circ}$ C.

Table 41. Analysis parameters of nuclear high temperature electrolysis based ammonia production system

LHV of Ammonia (kJ/kg)	18570
Mass of Nitrogen (kg)	0.823
Mass of Water (kg)	1.59
Mass of Ammonia (kg)	1
Required Electricity $W_{elec}$ (kWh)	7.12
Required Heat $Q_{in}$ (kWh)	1.18
Nuclear to Electricity Energy Efficiency $\eta_{en,\text{nuc.ht.elec.}}$ (%)	35
Nuclear to Electricity Exergy Efficiency $\eta_{ex,\text{nuc.ht.elec.}}$ (%)	30

#### Sustainability index (SI)

Sustainability index of nuclear high temperature electrolysis based ammonia production system can be defined as:

$$SI_{15} = \frac{1}{1 - \eta_{ex,15}}$$

# Improvement potential (IP)

Improvement potential of nuclear high temperature electrolysis based ammonia production system can be defined as:

 $IP_{15} = (1 - \eta_{ex,15}) \cdot (Exergy input - Exergy output)$ 

Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 15 are illustrated respectively.



# Fig.97 Abiotic depletion values of nuclear high temperature electrolysis based ammonia production method



Fig.98 Ozone layer depletion values of nuclear high temperature electrolysis based ammonia production method



Fig.99 Human toxicity values of nuclear high temperature electrolysis based ammonia production method

Table 42. Results of method 15				
Energy efficiency η <sub>en,15</sub> (%)	Exergy efficiency η <sub>ex,15</sub> (%)	Sustainability index SI <sub>15</sub>	Improvement Potential IP <sub>15</sub> (kJ)	
23.8	20.4	1.257	15,747	

# Biomass electrolysis based ammonia production (Method 16)

The cycle used is the conventional Rankine cycle with biomass being burned in a high pressure boiler to generate steam. The net power cycle efficiencies that can be achieved are about 23% to 34%. The exhaust of the steam turbine can either be fully condensed to produce power or used partly or fully for another useful heating activity. In addition to the exclusive use of biomass combustion to power a steam turbine, biomass can be co-fired with coal in a coal-fired power plant.


Fig.100. Ammonia production via biomass electrolysis

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.



Fig.101 Energy and material flows of biomass electrolysis based ammonia production

As illustrated in Fig. 101, the energy efficiency of biomass electrolysis based ammonia production system can be defined as:

$$\eta_{en,16} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{water} \cdot h_{water} + m_{nitrogen} \cdot h_{nitrogen} + \frac{W_{elec}}{\eta_{en,bio,e}}}$$

The exergy efficiency of biomass electrolysis based ammonia production system can be written as:

$$\eta_{ex,16} = \frac{m_{ammonia} \cdot ex_{ammonia}}{m_{water} \cdot ex_{water} + m_{nitrogen} \cdot ex_{nitrogen} + \frac{W_{elec}}{\eta_{ex,bio,e}}}$$

Table 43. Analysis parameters of biomass electrolysis based ammonia production system

LHV of Ammonia (kJ/kg)	18570
Mass of Nitrogen (kg)	0.823
Mass of Water (kg)	1.59
Mass of Ammonia (kg)	1
Required Electricity $W_{elec}$ (kWh)	11
Biomass to Electricity Energy Efficiency $\eta_{en,bio,e}$ (%)	33
Biomass to Electricity Exergy Efficiency $\eta_{ex,bio,e}$ (%)	30

# Sustainability index (SI)

Sustainability index of biomass electrolysis based ammonia production system can be defined as:

$$SI_{16} = \frac{1}{1 - \eta_{ex,16}}$$

#### **Improvement potential (IP)**

Improvement potential of biomass electrolysis based ammonia production system can be defined as:

$$IP_{16} = (1 - \eta_{ex,16}) \cdot (Exergy input - Exergy output)$$

## Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 16 are illustrated respectively.



Fig.102 Abiotic depletion values of biomass electrolysis based ammonia production method



Fig.103 Ozone layer depletion values of biomass electrolysis based ammonia production method



Fig.104 Human toxicity values of biomass electrolysis based ammonia production method

Table 44. Results of method 16			
Energy efficiency Exergy efficiency Sustainability index Improvement Potent			
η <sub>en,16</sub> (%)	η <sub>ex,16</sub> (%)	<b>SI</b> 16	IP <sub>16</sub> (kJ)
15.4	15.5	1.183	16,211

#### Bituminous coal electrolysis based ammonia production (Method 17)

Bituminous grade coal, is the primary coal used in electric generation (steam coal) and in metallurgy. About half of all the coal burned in the world is this grade. It ranges from 50-86% carbon content and any energy content above 6,400 kcal/kg. Alberta, Saskatchewan and Nova Scotia, for instance, who have large coal deposits, generate most of their electricity from coal. Ontario, because of its huge power needs, has a diverse electricity generation portfolio and gets about 15% of its electricity from coal.



Fig.105 Ammonia production via bituminous coal electrolysis

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.



Fig.106 Energy and material flows of bituminous coal electrolysis based ammonia production

As illustrated in Fig. 106, the energy efficiency of bituminous coal electrolysis based ammonia production system can be defined as:

$$\eta_{en,17} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{water} \cdot h_{water} + m_{nitrogen} \cdot h_{nitrogen} + \frac{W_{elec}}{\eta_{en,bit,coal}}}$$

The exergy efficiency of bituminous coal electrolysis based ammonia production system can be written as:

$$\eta_{ex,17} = \frac{m_{ammonia} \cdot ex_{ammonia}}{m_{water} \cdot ex_{water} + m_{nitrogen} \cdot ex_{nitrogen} + \frac{W_{elec}}{\eta_{ex,bit,coal}}}$$

Table 45. Analysis parameters of bituminous coal electrolysis based ammonia production system

LHV of Ammonia (kJ/kg)	18570
Mass of Nitrogen (kg)	0.823
Mass of Water (kg)	1.59
Mass of Ammonia (kg)	1
Required Electricity $W_{elec}$ (kWh)	11
Bituminous Coal to Electricity Energy Efficiency $\eta_{en,\text{bit,coal}}$ (%)	42
Bituminous Coal to Electricity Exergy Efficiency $\eta_{ex,bit,coal}$ (%)	39

# Sustainability index (SI)

Sustainability index of bituminous coal electrolysis based ammonia production system can be defined as:

$$SI_{17} = \frac{1}{1 - \eta_{ex,17}}$$

#### Improvement potential (IP)

Improvement potential of bituminous coal electrolysis based ammonia production system can be defined as:

$$IP_{17} = (1 - \eta_{ex,17}) \cdot (Exergy input - Exergy output)$$

# Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 17 are illustrated respectively.



Fig.107 Abiotic depletion values of bituminous coal electrolysis based ammonia production method



Fig.108 Ozone layer depletion values of bituminous coal electrolysis based ammonia production method



Fig.109 Human toxicity values of bituminous coal electrolysis based ammonia production method

Table 46. Results of method 17			
Energy efficiency η <sub>en,17</sub> (%)	Exergy efficiency η <sub>ex,17</sub> (%)	Sustainability index SI <sub>17</sub>	Improvement Potential IP17 (kJ)
19.6	20.1	1.252	15,321

# Coal electrolysis based ammonia production (Method 18)

In this method, hard coal is utilized. Final degree of carbonization leads to anthracite, "hard coal". With any carbon content greater than 86%, hard coal is the least common and therefore the most expensive grade of coal.



Fig.110. Ammonia production via coal electrolysis

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.



Fig.111. Energy and material flows of coal electrolysis based ammonia production

As illustrated in Fig. 111, the energy efficiency of coal electrolysis based ammonia production system can be defined as:

$$\eta_{en,18} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{water} \cdot h_{water} + m_{nitrogen} \cdot h_{nitrogen} + \frac{W_{elec}}{\eta_{en,coal,e}}}$$

The exergy efficiency of coal electrolysis based ammonia production system can be written as:

$$\eta_{ex,18} = \frac{m_{ammonia} \cdot ex_{ammonia}}{m_{water} \cdot ex_{water} + m_{nitrogen} \cdot ex_{nitrogen} + \frac{W_{elec}}{\eta_{ex,coal,e}}}$$

Table 47. Analysis parameters of coal electrolysis based ammonia production system

LHV of Ammonia (kJ/kg)	18570
Mass of Nitrogen (kg)	0.823
Mass of Water (kg)	1.59
Mass of Ammonia (kg)	1
Required Electricity $W_{elec}$ (kWh)	11
Coal to Electricity Energy Efficiency $\eta_{en,coal,e}$ (%)	40
Coal to Electricity Exergy Efficiency $\eta_{ex,coal,e}$ (%)	37

# Sustainability index (SI)

Sustainability index of coal electrolysis based ammonia production system can be defined as:

$$SI_{18} = \frac{1}{1 - \eta_{ex,18}}$$

# **Improvement potential (IP)**

Improvement potential of coal electrolysis based ammonia production system can be defined as:  $IP_{18} = (1 - \eta_{ex,18}) \cdot (Exergy input - Exergy output)$ 

# Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 18 are illustrated respectively.



Fig.112 Abiotic depletion values of coal electrolysis based ammonia production method



Fig.113 Ozone layer depletion values of coal electrolysis based ammonia production method



Fig.114 Human toxicity values of coal electrolysis based ammonia production method

Table 48. Results of method 18			
Energy efficiency η <sub>en.18</sub> (%)	Exergy efficiency η <sub>ex.18</sub> (%)	Sustainability index SI <sub>18</sub>	Improvement Potential IP <sub>18</sub> (kJ)
18.7	19.1	1.236	15,519

#### Heavy oil electrolysis based ammonia production (Method 19)

Oil, like the other fossil fuels, can be used for electricity generation. The process is the same as coal or natural gas power plants: the fuel is burned, heats water that turns into steam and spins a turbine.



Fig.115. Ammonia production via heavy oil electrolysis

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.



Fig.116 Energy and material flows of heavy oil electrolysis based ammonia production

As illustrated in Fig. 116, the energy efficiency of heavy oil electrolysis based ammonia production system can be defined as:

$$\eta_{en,19} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{water} \cdot h_{water} + m_{nitrogen} \cdot h_{nitrogen} + \frac{W_{elec}}{\eta_{en,heavy,e}}}$$

The exergy efficiency of heavy oil electrolysis based ammonia production system can be written as:

$$\eta_{ex,19} = \frac{m_{ammonia} \cdot ex_{ammonia}}{m_{water} \cdot ex_{water} + m_{nitrogen} \cdot ex_{nitrogen} + \frac{W_{elec}}{\eta_{ex,heavy,e}}}$$

Table 49. Analysis parameters of heavy oil electrolysis based ammonia production system

LHV of Ammonia (kJ/kg)	19570
Mass of Nitrogen (kg)	0.823
Mass of Water (kg)	1.59
Mass of Ammonia (kg)	1
Required Electricity $W_{elec}$ (kWh)	11
Heavy Oil to Electricity Energy Efficiency $\eta_{en,heavy,e}$ (%)	40
Heavy Oil to Electricity Exergy Efficiency $\eta_{ex,heavy,e}$ (%)	37

## Sustainability index (SI)

Sustainability index of heavy oil electrolysis based ammonia production system can be defined as:

$$SI_{19} = \frac{1}{1 - \eta_{ex,19}}$$

## **Improvement potential (IP)**

Improvement potential of heavy oil electrolysis based ammonia production system can be defined as:

 $IP_{19} = (1 - \eta_{ex,19}) \cdot (Exergy input - Exergy output)$ 

#### Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 19 are illustrated respectively.



Fig.117 Abiotic depletion values of heavy oil electrolysis based ammonia production method



Fig.118 Ozone layer depletion values of heavy oil electrolysis based ammonia production method



Fig.119 Human toxicity values of heavy oil electrolysis based ammonia production method

Table 50. Results of method 19			
Energy efficiency	Exergy efficiency	Sustainability index	<b>Improvement Potential</b>
η <sub>en,19</sub> (%)	η <sub>ex,19</sub> (%)	<b>SI</b> 19	IP <sub>19</sub> (kJ)
20.5	21.1	1.268	15,124

## Hydropower (reservoir type) electrolysis based ammonia production (Method 20)

Man-made dams retain massive amounts of water in reservoirs, and form drastic drop-offs that enhance the kinetic energy of falling water. Lifetime is assumed to be 150 years for the structural part and 80 years for the turbines.



Fig.120 Ammonia production via hydropower (reservoir type) electrolysis

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.



Fig.121 Energy and material flows of hydropower (reservoir type) electrolysis based ammonia production

As illustrated in Fig. 121, the energy efficiency of hydropower (reservoir type) electrolysis based ammonia production system can be defined as:

 $\eta_{en,20} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{water} \cdot h_{water} + m_{nitrogen} \cdot h_{nitrogen} + \frac{W_{elec}}{\eta_{en,hydro,r}}}$ 

The exergy efficiency of hydropower (reservoir type) electrolysis based ammonia production system can be written as:

$$\eta_{ex,20} = \frac{m_{ammonia} \cdot ex_{ammonia}}{m_{water} \cdot ex_{water} + m_{nitrogen} \cdot ex_{nitrogen} + \frac{W_{elec}}{\eta_{ex} \text{ bydrow}}}$$

Table 51. Analysis parameters of hydropower (reservoir type) electrolysis based ammonia production system

LHV of Ammonia (kJ/kg)	19570
Mass of Nitrogen (kg)	0.823
Mass of Water (kg)	1.59
Mass of Ammonia (kg)	1
Required Electricity $W_{elec}$ (kWh)	11
Hydropower (reservoir type) to Electricity Energy Efficiency $\eta_{en,hydro,r}$ (%)	78
Hydropower (reservoir type) to Electricity Exergy Efficiency $\eta_{ex,hydro,r}$ (%)	77

# Sustainability index (SI)

Sustainability index of hydropower (reservoir type) electrolysis based ammonia production system can be defined as:

$$SI_{20} = \frac{1}{1 - \eta_{ex,20}}$$

# **Improvement potential (IP)**

Improvement potential of hydropower (reservoir type) electrolysis based ammonia production system can be defined as:

 $IP_{20} = (1 - \eta_{ex,20}) \cdot (Exergy input - Exergy output)$ 

# Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 20 are illustrated respectively.







Fig.123 Ozone layer depletion values of hydropower (reservoir type) electrolysis based ammonia production method



Fig.124 Human toxicity values of hydropower (reservoir type) electrolysis based ammonia production method

Table 52. Results of method 20			
Energy efficiency	Exergy efficiency	Sustainability index	Improvement Potential
<u>η<sub>en,20</sub> (%)</u>	η <sub>ex,20</sub> (%)	SI <sub>20</sub>	IP <sub>20</sub> (kJ)
36.3	39.7	1.659	11,563

#### Hydropower (on river) electrolysis based ammonia production (Method 21)

Run-of-river facilities employ the natural flow and elevation drop of rivers. An intake structure forces water through a submerged pipeline, or penstock, which leads to a turbine. The turbine drives a generator, which then produces alternating current. Lifetime is assumed to be 80 years. Net average efficiency is 82%



Fig.125 Ammonia production via hydropower (on river) electrolysis

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.



Fig.126 Energy and material flows of hydropower (on river) electrolysis based ammonia production

As illustrated in Fig. 126, the energy efficiency of hydropower (on river) electrolysis based ammonia production system can be defined as:

$$\eta_{en,21} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{water} \cdot h_{water} + m_{nitrogen} \cdot h_{nitrogen} + \frac{W_{elec}}{\eta_{en,hydro,river}}}$$

The exergy efficiency of hydropower (on river) electrolysis based ammonia production system can be written as:

n –	$m_{ammonia} \cdot ex_{ammonia}$	
$\eta_{ex,21} -$	$m \rightarrow ar + m \rightarrow ar \rightarrow ar$	W <sub>elec</sub>
	mwater <sup>Ex</sup> water <sup>†</sup> <sup>m</sup> nitrogen <sup>Ex</sup> nitrogen	$\eta_{ar}$ hydro river

Table 53. Analysis parameters of hydropower (on river) electrolysis based ammonia production system

LHV of Ammonia (kJ/kg)	19570
Mass of Nitrogen (kg)	0.823
Mass of Water (kg)	1.59
Mass of Ammonia (kg)	1
Required Electricity W <sub>elec</sub> (kWh)	11
Hydropower (on river) to Electricity Energy Efficiency $\eta_{en,hydro,river}$ (%)	82
Hydropower (on river) to Electricity Exergy Efficiency $\eta_{ex,hydro,river}$ (%)	80

#### Sustainability index (SI)

Sustainability index of hydropower (on river) electrolysis based ammonia production system can be defined as:

$$SI_{21} = \frac{1}{1 - \eta_{ex,21}}$$

#### **Improvement potential (IP)**

Improvement potential of hydropower (on river) electrolysis based ammonia production system can be defined as:

 $IP_{21} = (1 - \eta_{ex,21}) \cdot (Exergy input - Exergy output)$ 

#### Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 21 are illustrated respectively.







Fig.128 Ozone layer depletion values of hydropower (on river) electrolysis based ammonia production method



Fig.129 Human toxicity values of hydropower (on river) electrolysis based ammonia production method

Table 54. Results of method 21				
Energy efficiency n <sub>en 21</sub> (%)	Exergy efficiency η <sub>ex 21</sub> (%)	Sustainability index SI21	Improvement Potential IP21 (kJ)	
38.1	41.3	1.702	11,266	

#### Municipal waste electrolysis based ammonia production (Method 22)

Electricity can be produced by burning municipal solid waste as a fuel. Waste used in the calculations contains 21% paper, 8% Mixed cardboard, 15% plastics, 3% laminated materials, 2% laminated packaging, e.g. tetra bricks, 3% combined goods: dipers; 3% glass, 2% textiles, 8% minerals, 9% natural products, 22% compostable material, 2.65% inert metals, 1% volatile metals, 0.0065% batteries, 0.34% electronic goods. Lower heating value is 11.74 MJ/kg and thermal efficiency is taken as 25%.



Fig.130 Ammonia production via municipal waste electrolysis

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.





As illustrated in Fig. 131, the energy efficiency of municipal waste electrolysis based ammonia production system can be defined as:

$$\eta_{en,22} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{water} \cdot h_{water} + m_{nitrogen} \cdot h_{nitrogen} + \frac{W_{elec}}{\eta_{en,municipal}}}$$

The exergy efficiency of municipal waste electrolysis based ammonia production system can be written as:

$$\eta_{ex,22} = \frac{m_{ammonia} \cdot ex_{ammonia}}{m_{water} \cdot ex_{water} + m_{nitrogen} \cdot ex_{nitrogen} + \frac{W_{elec}}{\eta_{ex,municipal}}}$$

	pro anton on o jou
LHV of Ammonia (kJ/kg)	19570
Mass of Nitrogen (kg)	0.823
Mass of Water (kg)	1.59
Mass of Ammonia (kg)	1
Required Electricity $W_{elec}$ (kWh)	11
Municipal waste to Electricity Energy Efficiency $\eta_{en,\text{municipal}}$ (%)	25
Municipal waste to Electricity Exergy Efficiency $\eta_{ex,municipal}$ (%)	20

Table 55. Analysis parameters of municipal waste electrolysis based ammonia production system

## Sustainability index (SI)

Sustainability index of municipal waste electrolysis based ammonia production system can be defined as:

$$SI_{22} = \frac{1}{1 - \eta_{ex,22}}$$

## **Improvement potential (IP)**

Improvement potential of municipal waste electrolysis based ammonia production system can be defined as:

 $IP_{22} = (1 - \eta_{ex,22}) \cdot (Exergy input - Exergy output)$ 

## Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 22 are illustrated respectively.



Fig.132 Abiotic depletion values of municipal waste electrolysis based ammonia production method



Fig.133 Ozone layer depletion values of municipal waste electrolysis based ammonia production method



Fig.134 Human toxicity values of municipal waste electrolysis based ammonia production method

Table 56. Results of method 22				
Energy efficiency	Exergy efficiency	Sustainability index	<b>Improvement Potential</b>	
η <sub>en,22</sub> (%)	η <sub>ex,22</sub> (%)	$SI_{22}$	IP <sub>22</sub> (kJ)	
11.7	10.31	1.115	17,200	

# Natural gas electrolysis based ammonia production (Method 23)

Of the total electricity generated in Canada, approximately 5% (31 million MWh) can be attributed to the combustion of natural gas.



Fig.135 Ammonia production via natural gas electrolysis

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.



Fig.136 Energy and material flows of natural gas electrolysis based ammonia production

As illustrated in Fig. 136, the energy efficiency of natural gas electrolysis based ammonia production system can be defined as:

 $\eta_{en,23} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{water} \cdot h_{water} + m_{nitrogen} \cdot h_{nitrogen} + \frac{W_{elec}}{\eta_{en,ng}}}$ 

The exergy efficiency of natural gas electrolysis based ammonia production system can be written as:

$$\eta_{ex,23} = \frac{m_{ammonia} \cdot ex_{ammonia}}{m_{water} \cdot ex_{water} + m_{nitrogen} \cdot ex_{nitrogen} + \frac{W_{elec}}{\eta_{ex,ng}}}$$

Table 57. Analysis parameters of natural gas electrolysis based ammonia production system

LHV of Ammonia (kJ/kg)	19570
Mass of Nitrogen (kg)	0.823
Mass of Water (kg)	1.59
Mass of Ammonia (kg)	1
Required Electricity $W_{elec}$ (kWh)	11
Natural gas to Electricity Energy Efficiency $\eta_{en,ng}$ (%)	35
Natural gas to Electricity Exergy Efficiency $\eta_{ex,ng}$ (%)	30

#### Sustainability index (SI)

Sustainability index of natural gas electrolysis based ammonia production system can be defined as:

$$SI_{23} = \frac{1}{1 - \eta_{ex,23}}$$

#### **Improvement potential (IP)**

Improvement potential of natural gas electrolysis based ammonia production system can be defined as:

 $IP_{23} = (1 - \eta_{ex,23}) \cdot (Exergy input - Exergy output)$ 

#### Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 23 are illustrated respectively.



Fig.137 Abiotic depletion values of natural gas electrolysis based ammonia production method



Fig.138 Ozone layer depletion values of natural gas electrolysis based ammonia production method



Fig.139 Human toxicity values of natural gas electrolysis based ammonia production method

Table 58. Results of method 23					
Energy efficiency	Exergy efficiency	Sustainability index	<b>Improvement Potential</b>		
η <sub>en,23</sub> (%)	η <sub>ex,23</sub> (%)	<b>SI</b> 23	IP <sub>23</sub> (kJ)		
16.4	15.5	1.183	16,211		

Table 58.	Results	of method	23
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## Nuclear 3 step CuCl cycle based based ammonia production (Method 24)

The copper-chlorine cycle (CuCl cycle) is a multiple step thermochemical cycle for the production of hydrogen. The CuCl cycle is a hybrid process that employs both thermochemical and electrolysis steps. The CuCl cycle involves four chemical reactions for water splitting, whose net reaction decomposes water into hydrogen and oxygen.

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.



Fig.140 Energy and material flows of nuclear 3 step CuCl cycle based ammonia production

As illustrated in Fig. 140, the energy efficiency of nuclear 3 step CuCl cycle based ammonia production system can be defined as:

$$\eta_{en,24} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{water} \cdot h_{water} + m_{nitrogen} \cdot h_{nitrogen} + \frac{W_{elec}}{\eta_{en,nuc,3}} + Q_{in}}$$

The exergy efficiency of nuclear 3 step CuCl cycle based ammonia production system can be written as:

$$\eta_{ex,24} = \frac{m_{ammonia} \cdot ex_{ammonia}}{m_{water} \cdot ex_{water} + m_{nitrogen} \cdot ex_{nitrogen} + \frac{W_{elec}}{\eta_{ex,nuc,3}} + Q_{in} \left(\frac{T}{T_0} - 1\right)}$$

Here, temperature T is taken as  $500^{\circ}$ C.

Table 59 Analysis parameters of nuclear 3 step CuCl cycle based ammonia production system	
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LHV of Ammonia (kJ/kg)	18570
Mass of Nitrogen (kg)	0.823
Mass of Water (kg)	1.59
Mass of Ammonia (kg)	1
Required Electricity $W_{elec}$ (kWh)	3.30
Required Heat $Q_{in}$ (kWh)	8.98
Nuclear to Electricity Energy Efficiency $\eta_{en,\mathrm{nuc},3}$ (%)	43
Nuclear to Electricity Exergy Efficiency $\eta_{ex,nuc,3}$ (%)	38

#### Sustainability index (SI)

Sustainability index of nuclear 3 step CuCl cycle based ammonia production system can be defined as

$$SI_{24} = \frac{1}{1 - \eta_{ex,24}}$$

# **Improvement potential (IP)**

Improvement potential of nuclear 3 step CuCl cycle based ammonia production system can be defined as:

$$IP_{24} = (1 - \eta_{ex,24}) \cdot (Exergy input - Exergy output)$$

# Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 24 are illustrated respectively.



Fig.141 Abiotic depletion values of nuclear 3 step CuCl cycle based ammonia production method



Fig.142 Ozone layer depletion values of nuclear 3 step CuCl cycle based ammonia production method





Table 60. Results of method 24				
Energy efficiency η <sub>en,24</sub> (%)	Exergy efficiency η <sub>ex,24</sub> (%)	Sustainability index SI <sub>24</sub>	Improvement Potential IP <sub>24</sub> (kJ)	
30.8	17.8	1.216	61,930	

## Nuclear 4 step CuCl cycle based ammonia production (Method 25)

The CuCl process can be linked with nuclear plants or other heat sources such as solar and industrial waste heat to potentially achieve higher efficiencies, lower environmental impact and lower costs of hydrogen production than any other conventional technology.

#### **Efficiency assessment**

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.



Fig.144 Energy and material flows of nuclear 4 step CuCl cycle based ammonia production

As illustrated in Fig. 144, the energy efficiency of nuclear 4 step CuCl cycle based ammonia production system can be defined as:

$$\eta_{en,25} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{water} \cdot h_{water} + m_{nitrogen} \cdot h_{nitrogen} + \frac{W_{elec}}{\eta_{en,nuc,4}} + Q_{in}}$$

The exergy efficiency of nuclear 4 step CuCl cycle based ammonia production system can be written as:

$$\eta_{ex,25} = \frac{m_{ammonia} \cdot ex_{ammonia}}{m_{water} \cdot ex_{water} + m_{nitrogen} \cdot ex_{nitrogen} + \frac{W_{elec}}{\eta_{ex,nuc,4}} + Q_{in} \left(\frac{T}{T_0} - 1\right)}$$

Here, temperature T is taken as 500°C.

Table 61. Analysis	parameters of nuclear 4	step CuCl cy	vele based ammor	nia production s	vstem
2				1	2

LHV of Ammonia (kJ/kg)	18570
Mass of Nitrogen (kg)	0.823
Mass of Water (kg)	1.59
Mass of Ammonia (kg)	1
Required Electricity $W_{elec}$ (kWh)	3.30
Required Heat $Q_{in}$ (kWh)	7.92
Nuclear to Electricity Energy Efficiency $\eta_{en,\mathrm{nuc},4}$ (%)	44
Nuclear to Electricity Exergy Efficiency $\eta_{ex.nuc.4}$ (%)	39

## Sustainability index (SI)

Sustainability index of nuclear 4 step CuCl cycle based ammonia production system can be defined as:

$$SI_{25} = \frac{1}{1 - \eta_{ex,25}}$$

## **Improvement potential (IP)**

Improvement potential of nuclear 4 step CuCl cycle based ammonia production system can be defined as:

 $IP_{25} = (1 - \eta_{ex,25}) \cdot (Exergy input - Exergy output)$ 

# Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 25 are illustrated respectively.



Fig.145 Abiotic depletion values of nuclear 4 step CuCl cycle based ammonia production method



Fig.146 Ozone layer depletion values of nuclear 4 step CuCl cycle based ammonia production method



Fig.147 Human toxicity values of nuclear 4 step CuCl cycle based ammonia production method

Table 62. Results of method 25				
Energy efficiency η <sub>en,25</sub> (%)	Exergy efficiency η <sub>ex,25</sub> (%)	Sustainability index SI25	Improvement Potential IP <sub>25</sub> (kJ)	
33.2	19.6	1.243	52,573	

#### Nuclear 5 step CuCl cycle based ammonia production (Method 26)

In the 5 step cycle, copper is produced electrolytically, moved to an exothermic thermo-chemical hydrogen reactor and then reacted with HCl gas to produce hydrogen gas and molten CuCl. The overall efficiency of the CuCl cycle is potentially much higher than conventional water electrolysis via thermal power plants, since heat is used directly to produce hydrogen, rather than indirectly to first produce electricity, after which hydrogen is generated.

#### **Efficiency assessment**

Based on the inputs and outputs of the system, energy and exergy efficiency definitions are determined and efficiency calculations are conducted using EES software.



Fig.148 Energy and material flows of nuclear 5 step CuCl cycle based ammonia production

As illustrated in Fig. 148, the energy efficiency of nuclear 5 step CuCl cycle based ammonia production system can be defined as;

$$\eta_{en,26} = \frac{m_{ammonia} \cdot LHV_{ammonia}}{m_{water} \cdot h_{water} + m_{nitrogen} \cdot h_{nitrogen} + \frac{W_{elec}}{\eta_{en,nuc,5}} + Q_{in}}$$

The exergy efficiency of nuclear 5 step CuCl cycle based ammonia production system can be written as:

$$\eta_{ex,26} = \frac{m_{ammonia} \cdot ex_{ammonia}}{m_{water} \cdot ex_{water} + m_{nitrogen} \cdot ex_{nitrogen} + \frac{W_{elec}}{\eta_{ex,nuc,5}} + Q_{in} \left(\frac{T}{T_0} - 1\right)$$

Here, temperature T is taken as 500°C.

Table 63. Analysis parameters of nuclear 5 step CuCl cycle based ammonia production system

LHV of Ammonia (kJ/kg)	18570
Mass of Nitrogen (kg)	0.823
Mass of Water (kg)	1.59
Mass of Ammonia (kg)	1
Required Electricity $W_{elec}$ (kWh)	2.47
Required Heat $Q_{in}$ (kWh)	9.61
Nuclear to Electricity Energy Efficiency $\eta_{en,\text{nuc},5}$ (%)	45
Nuclear to Electricity Exergy Efficiency $\eta_{ex,nuc,5}$ (%)	40

## Sustainability index (SI)

Sustainability index of nuclear 5 step CuCl cycle based ammonia production system can be defined as:

$$SI_{26} = \frac{1}{1 - \eta_{ex,26}}$$

# **Improvement potential (IP)**

Improvement potential of nuclear 5 step CuCl cycle based ammonia production system can be defined as:

 $IP_{26} = (1 - \eta_{ex,26}) \cdot (Exergy input - Exergy output)$ 

## Life cycle assessment analysis

Abiotic depletion, ozone depletion layer and human toxicity values of method 26 are illustrated respectively.

Table 64. Results of method 26							
Energy efficiency	Exergy efficiency	Sustainability index	Improvement Potential				
η <sub>en,26</sub> (%)	η <sub>ex,26</sub> (%)	SI <sub>26</sub>	IP <sub>26</sub> (kJ)				
33.9	18.2	1.223	64,037				



Fig.149 Abiotic depletion values of nuclear 5 step CuCl cycle based ammonia production method



Fig.150 Ozone layer depletion values of nuclear 5 step CuCl cycle based ammonia production method



Fig.151 Human toxicity values of nuclear 5 step CuCl cycle based ammonia production method



#### Overall life cycle, cost, sustainability, efficiency improvement potential comparison of various ammonia production methods

Fig.152 Overall single score comparison of ammonia production methods according to Eco-Indicator 99



Fig.153 Damage assessment (relative) results of all ammonia production methods according to Eco-Indicator 99

Method Nr.	Method	Energy efficiency η <sub>en</sub> (%)	Exergy efficiency η <sub>ex</sub> (%)	Sustainability index SI	Improvement Potential IP (kJ)
1	Steam methane reforming	27	22	1.282	56,386
2	Wind	18.6	18	1.22	15,717
3	Solar	9.4	7.7	1.084	17,695
4	UCG	39.6	41.9	1.721	12,849
5	UCG with CCS	35.7	37.5	1.601	15,016
6	Biomass DG	30	29.1	1.412	35,091
7	Biomass CFBG	29.4	28.8	1.405	35,853
8	Tidal & Waves	39.5	41.3	1.702	11,266
9	Coal gasification	23.3	23.9	1.314	45,357
10	Geothermal	16.6	10.31	1.115	17,200
11	Hydropower	42.7	46.4	1.866	10,277
12	OTEC	3.3	3	1.032	18,585
13	Nuclear based electrolysis	16.4	15.5	1.183	16,211
14	Heavy oil partial oxidation	35	36	1.561	22,292
15	Nuclear high temperature electrolysis	23.8	20.4	1.257	15,747

Table 65. Results of all ammonia production methods

16	Biomass based electrolysis	15.4	15.5	1.183	16,211
17	Bituminous coal fired based electrolysis	19.6	20.1	1.252	15,321
18	Coal fired based electrolysis	18.7	19.1	1.236	15,519
19	Heavy oil based electrolysis	20.5	21.1	1.268	15,124
20	Hydropower (Reservoir) electrolysis	36.3	39.7	1.659	11,563
21	Hydropower (on river) electrolysis	38.1	41.3	1.702	11,266
22	Municipal waste based electrolysis	11.7	10.31	1.115	17,200
23	Natural gas based electrolysis	16.4	15.5	1.183	16,211
24	Nuclear 3 step CuCl cycle	30.8	17.8	1.216	61,930
25	Nuclear 4 step CuCl cycle	33.2	19.6	1.243	52,573
26	Nuclear 5 step CuCl cycle	33.9	18.2	1.223	64,037


Fig.154 Energy efficiency results of all ammonia production methods



Fig.155 Exergy efficiency results of all ammonia production methods



Sustainability index SI

Fig.156 Sustainability index results of all ammonia production methods

Hydropower

UCG

- Hydropower (on river) electrolysis
- Tidal & Waves
- Hydropower (Reservoir) electrolysis

UCG with CCS

Heavy oil partial oxidation

Biomass DG

- Biomass CFBG
- Coal gasification
- Steam methane reforming
- Heavy oil based electrolysis
- Nuclear high temperature electrolysis
- Bituminous coal fired based electrolysis
- Nuclear 4 step CuCl cycle
- Coal fired based electrolysis
- Nuclear 5 step CuCl cycle

## Wind

- Nuclear 3 step CuCl cycle
- Natural gas based electrolysis
- Biomass based electrolysis
- Nuclear based electrolysis
- Municipal waste based electrolysis
- Geothermal
- Solar
- OTEC



Fig.157 Specific sustainability ratios of all ammonia production methods



Fig.158 Improvement potential results of all ammonia production methods



COMPARING PRODUCT STAGES; METHOD: ECO-INDICATOR 99 (E) V2.08 / EUROPE EI 99 E/E / SINGLE SCORE

Fig.159 Single score values of conventional ammonia production methods according to Eco-Indicator 99

- Ammonia from Bituminous Coal Electrolysis
- Ammonia from Heavy Oil Electrolysis
- Ammonia from Natural Gas Electrolysis
- Ammonia from Nuclear 4 Step Cu-Cl Cycle
- Ammonia from Nuclear Electrolysis
- Ammonia from Partial Oxidation of Heavy Oil
- Ammonia from UCG with CCS

Ammonia from Coal Gasification

- Ammonia from Coal Electrolysis
- Ammonia from Naphta Cracking
- Ammonia from Nuclear 3 Step Cu-Cl Cycle
- Ammonia from Nuclear 5 Step Cu-Cl Cycle
- Ammonia from Nuclear High Temperature Electrolysis
- Ammonia from SMR
- Ammonia from UCG without CCS







Fig.163 Abiotic depletion values of renewable ammonia production methods



Fig.164 Global warming values of renewable ammonia production methods



Fig.165 Climate change values of renewable ammonia production methods according to Eco-Indicator 99



Fig.166 Acidification/ Eutrophication values of renewable ammonia production methods according to Eco-Indicator 99



Ammonia from Coal Electrolysis

Ammonia from Nuclear Electrolysis

Ammonia from Naphta Cracking



Fig.167 Climate change values of conventional ammonia production methods according to Eco-Indicator 99



Fig.168 Acidification/ Eutrophication values of conventional ammonia production methods according to Eco-Indicator 99



Fig.169 Abiotic depletion values of all ammonia production methods according to Eco-Indicator 99







Fig.171 Human toxicity values of all ammonia production methods

Plant type	LCOE (\$/kWh)	Electricity consumption (kWh/kg)	Cost of ammonia (\$/kg)
Conventional Coal	0.0951	11	1.0461
Advanced Coal	0.1157	11	1.2727
Advanced Coal with CCS	0.1444	11	1.5884
Conventional Combined Cycle	0.0752	11	0.8272
Advanced Combined Cycle	0.0726	11	0.7986
Advanced Combined Cycle with CCS	0.1002	11	1.1022
Conventional Combustion Turbine	0.1415	11	1.5565
Advanced Combustion Turbine	0.1135	11	1.2485
Advanced Nuclear	0.0952	11	1.0472
Geothermal	0.0478	11	0.5258
Biomass	0.1005	11	1.1055
Wind	0.0736	11	0.8096
Wind – Offshore	0.1969	11	2.1659
Solar PV	0.1253	11	1.3783
Solar Thermal	0.2397	11	2.6367
Hydroelectric	0.0835	11	0.9185

Table 66. Cost of ammonia production from various sources based on Haber-Bosch and Electrolysis



Fig.172 Comparison of ammonia costs based on various sources by Haber-Bosch and electrolysis process

## Conclusions

The following concluding remarks are stated:

- LCA is an important and reliable tool to study ammonia production analysis and assessment as it covers the period from cradle to grave.
- Hydroelectric and wind energy based ammonia production yield lower production costs among other renewable resources.
- Having advanced and mature technology, natural gas combined cycle based ammonia production brings lower costs.
- In terms of human toxicity, coal and heavy oil fired power plant based electrolysis methods have highest values.
- Tidal&Waves, municipal waste and geothermal based ammonia production have lowest abiotic depletion, global warming and human toxicity values respectively among all methods.
- Coal gasification based ammonia production methods have lower acidification/ eutrophication values among conventional ammonia production methods.
- Nuclear electrolysis and naphtha cracking based ammonia production methods have least effect on climate change among conventional methods while Tidal&Waves method is the most environmentally benign method in terms of climate change and global warming.
- Solar PV based ammonia production has a close cost with coal based ammonia production.
- Current capabilities and efficiencies of Solar PV brings important environmental impact in terms of acidification, eutrophication and human toxicity because of manufacturing processes.
- Nuclear CuCl thermochemical cycles have highest improvement potentials.
- Hydropower, UCG and Tidal&Waves methods bring higher sustainability.
- Having very high energy conversion efficiencies, hydropower based ammonia production methods yield better energetic and exergetic performances together with UCG methods.
- The renewable sources with their improved efficiency can reduce the overall environmental footprint and can replace the current fossil fuel based centralized ammonia production facilities.
- As the cost of renewable electricity catches the level of conventional electricity, renewable energy based ammonia production systems will continue to gain practicality and popularity.
- Among novel ammonia production methods, molten salt based electrochemical ammonia synthesis together with SSAS arise as more reliable and promising in terms of practicality and scalability.
- Based on the results within this study, partner organizations will define specific methods for further evaluation focusing on actual business cases in Canada in order to analyze the cost, return of investment and thermodynamic behavior of the selected systems.

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