SPECIFIC REPORT

Natural Gas to Ammonia as a Potential Solution for British Columbia

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Abstract

Ammonia is projected to be a potential energy solution with high hydrogen content in the near future. In recent years, expectations are rising for hydrogen and ammonia as a medium for storage and transportation of energy in the mass introduction and use of renewable energy. Both storage and transport of hydrogen are considered 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 processes. Hydrogen carriers include ammonia synthesized from nitrogen and hydrogen that can be used for direct combustion. Ammonia becomes an important energy 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 produces mainly water and nitrogen on combustion, replacing a part of conventional fuel with ammonia will have a large effect in reducing carbon dioxide emissions.

Ammonia as a sustainable fuel can be used in all types of combustion engines, gas turbines, burners with only small modifications and directly in fuel cells which is a very important advantage compared to other type of fuels. In an ammonia economy, the availability of a pipeline to the residential area could supply ammonia to fuel cells, stationary generators, furnaces/boilers and vehicles which will bring a non-centralized power generation and enable a greener world. It is emphasized that the physical characteristics of ammonia is similar to propane. Besides having a significant advantages in storing and transporting natural gas, ammonia may also be burned directly in internal combustion engines. Compared to natural gas vehicles, ammonia-fueled vehicles do not produce direct CO_2 emission during operation.

Various pathways are investigated for cleaner utilization of fossil fuels especially natural gas. Ammonia is a carbon-free chemical energy carrier suitable for use as a transportation fuel. Furthermore, ammonia has a high octane rating (110–130), can be thermally cracked to produce hydrogen fuel using only about 12-15% of the higher heating value. It has a well-established production and distribution infrastructure, and has zero global warming potential (GWP). In addition to its attractive qualities as a fuel, ammonia is widely used as a NO_x reducing agent for combustion exhaust gases using selective catalytic reduction (SCR), and its capacity as a refrigerant can be applied to recover and further utilize engine heat that would otherwise be lost.

1. Introduction

The decarbonisation of fossil fuels, particularly, natural gas, is a promising alternative and compromises definite benefits over the use of carbon capture storage (CCS) technologies. Methane decarbonisation by pyrolysis also called as methane cracking includes the dissociation of methane (CH_4) into its molecular particles: solid carbon (C) and hydrogen (H_2). Its key benefit lies in the lack of CO/CO_2 emissions. Conversely to CCS, it substitutes the managing of CO_2 with a much lower quantity of easier-to-handle solid carbon. Hydrogen signifies a significant clean energy carrier, with an already substantial demand and capable projections for the future energy system. Moreover, carbon is hypothetically marketable as a product for both current and envisaged usages such as carbon fibres, materials and nanotechnology.

Compared to natural gas, there are more environmentally friendly fuels such as ammonia. Ammonia does not emit direct greenhouse gas emissions when utilized in the vehicles. Furthermore, production process of ammonia yields lower environmental impacts compared to natural gas production. Ammonia, which is a sustainable and clean fuel, can also be produced from natural gas and hydrocarbons. Henceforth, in the ideal case, if stranded natural gas reserves in British Columbia can be converted into ammonia and then transported via pipelines/trucks/ocean tankers to the ports, it would have lower total environmental impact both in the production process and utilization process. Furthermore, ammonia is liquid at higher temperatures (-33°C) than natural gas (-162°C) which implies lower energy requirement in liquefaction process of natural gas (Bicer and Dincer, 2015)

The other option for a more environmentally friendly process can be conversion of LNG to ammonia after being produced and transported via pipelines. Natural gas can be cracked into carbon black and hydrogen using hydrocarbon disassociation technique. In this case, carbon black is also utilized as a useful output for tire, plastic etc. industry. Instead of emitting CO_2 to the environment, produced carbon black is used for various sectors, and greenhouse gas emissions are lowered. Produced hydrogen can be used for ammonia synthesis and stored in the vessels for the overseas transportation. In this manner, a cleaner alternative fuel is consumed and total greenhouse gas emissions are significantly decreased. Henceforth, establishing an ammonia production plant using either tidal energy or hydropower electricity where British Columbia has significant potentials would be more environmentally friendly. As seen in Fig. 1, natural gas is already the primary source of ammonia production in the world using steam methane reforming method.

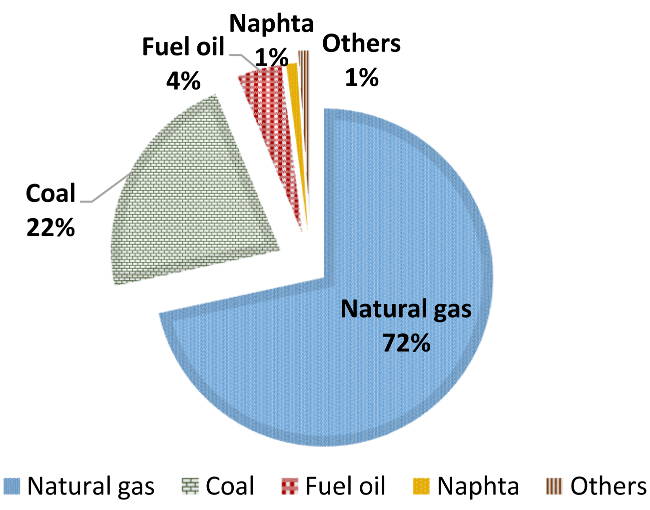

Fig.1. Sources of global ammonia production based on feedstock use (data from IEA, 2012)

Ammonia (NH_3):

- consists of one nitrogen atom from air separation and three hydrogen atoms from any conventional or renewable resources.
- is the second largest synthesized industrial chemical in the world.
- is a significant hydrogen carrier, transportation fuel, power generating fuel that does not contain any carbon atoms and has a high hydrogen ratio.
- does not emit direct greenhouse gas emission during utilization
- can be used as solid and/or liquid for many purposes.
- can be stored and transported under relatively lower pressures.
- can be produced from various type of resources ranging from natural gas to renewables.
- is a suitable fuel to be transferred using steel pipelines with minor modifications which are currently used for natural gas and oil.
- can be used in all types of combustion engines, gas turbines, burners as a sustainable fuel with only small modifications and directly in fuel cells which is a very important advantage compared to other type of fuels.
- brings a non-centralized power generation via fuel cells, stationary generators, furnaces/boilers and enables smart grid applications.
- can be used as a refrigerant for cooling in the car.

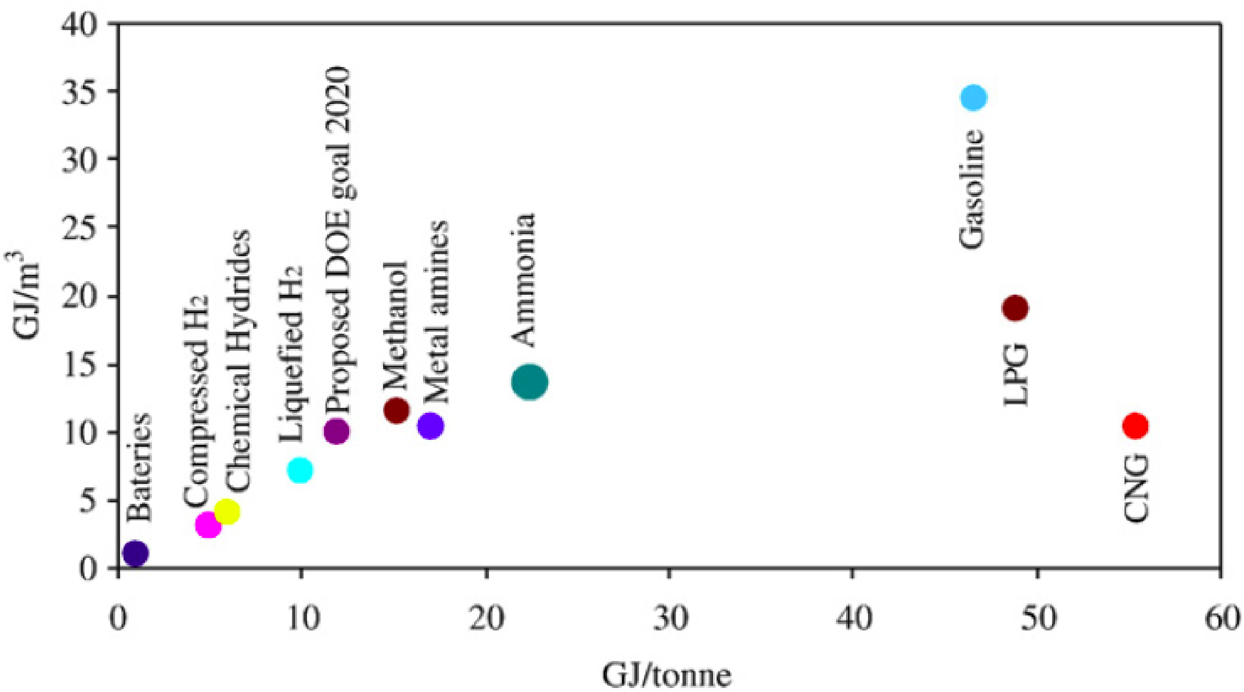

Fig. 2. Comparison of volumetric energy densities and specific energy densities of various fuels and ammonia (data from Zamfirescu and Dincer, 2008-2010)

Table 1. Comparison of ammonia with other fuels including natural gas

Fuel/storage	P [bar]	ρ Density [kg/m³]	HHV [MJ/kg]	HHV‴ [GJ/m³]	e‴ [GJ/m³]	c [CN$/kg]	C‴ [CN$/m³]	c/HHV [CN$/GJ]
Gasoline, C_8H_{18}/liquid	1	736	46.7	34.4	34.4	1.36	1000	29.1
CNG, CH_4/integrated storage	250	188	42.5	10.4	7.8	1.2	226	28.2
LPG, C_3H_8/pressurized tank	14	388	48.9	19	11.7	1.41	548	28.8
Methanol, CH_3OH/liquid	1	786	14.3	11.2	9.6	0.54	421	37.5
Hydrogen, H_2/metal hydrides	14	25	142	3.6	3	4	100	28.2
Ammonia, NH_3/pressurized tank	10	603	22.5	13.6	11.9	0.3	181	13.3
Ammonia, NH_3/metal amines	1	610	17.1	10.4	8.5	0.3	183	17.5

Source: Zamfirescu and Dincer, 2009

Table 1 and Fig. 2 imply that the energy density of ammonia is higher per unit volume compared to CNG. In addition, per unit energy, ammonia yields lower costs as seen in Table 1.

Ammonia can be produced from any hydrogen including hydrocarbons using cracking of hydrocarbons into hydrogen and carbon. Methane is a favored option for hydrogen production from a hydrocarbon because of its high H to C ratio, availability and low cost. Furthermore, microwave disassociation of methane is a promising option for cleaner ammonia production. Methane is separated into carbon black and hydrogen. The carbon 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 carbon requires much less development than sequestering gaseous CO_2.

Ammonia can also be produced from steam reforming of methane which is a little more energy intensive method. Steam methane reforming is the conversion of methane and water vapor into hydrogen and carbon monoxide which is an endothermic reaction. The heat can be supplied from the combustion of the methane feed gas. The process temperature and pressure values are generally 700 to 850°C and pressures of 3 to 25 bar, respectively.

In addition, renewable resources such as hydropower and tidal energy based power plants can be utilized for electricity requirements of ammonia production plants where there is a high potential in British Columbia

There are several technological options for methane dissociation to hydrogen and carbon, which are summarized in Fig. 3. British Columbia has huge potentials of hydropower which can be utilized in ammonia production process from natural gas as it is illustrated in Fig. 4. Produced ammonia can be used in power plants, vehicles and also household furnaces.

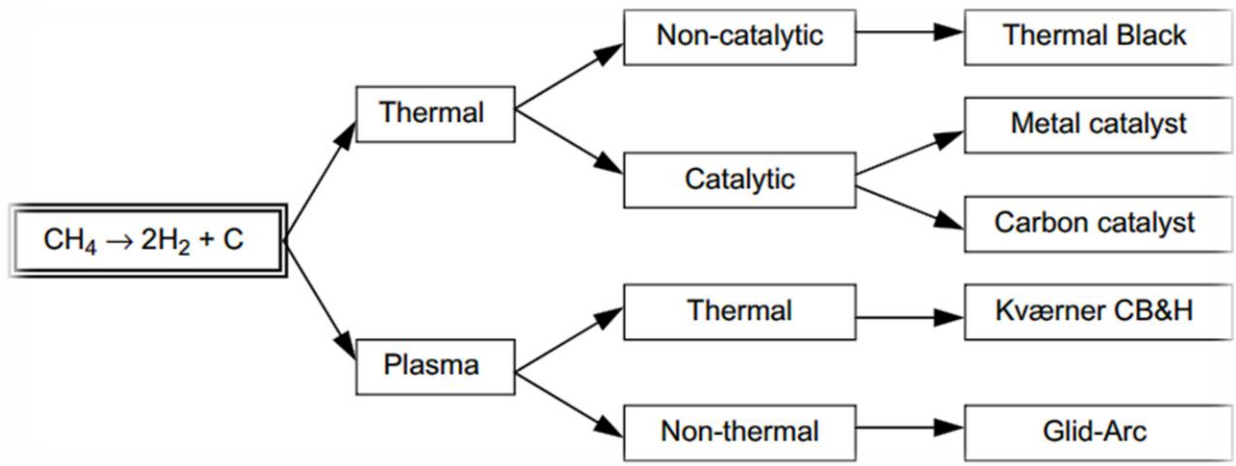

Fig. 3. Main routes for decomposition of methane to hydrogen and carbon (Muradov and Veziroğlu, 2008)

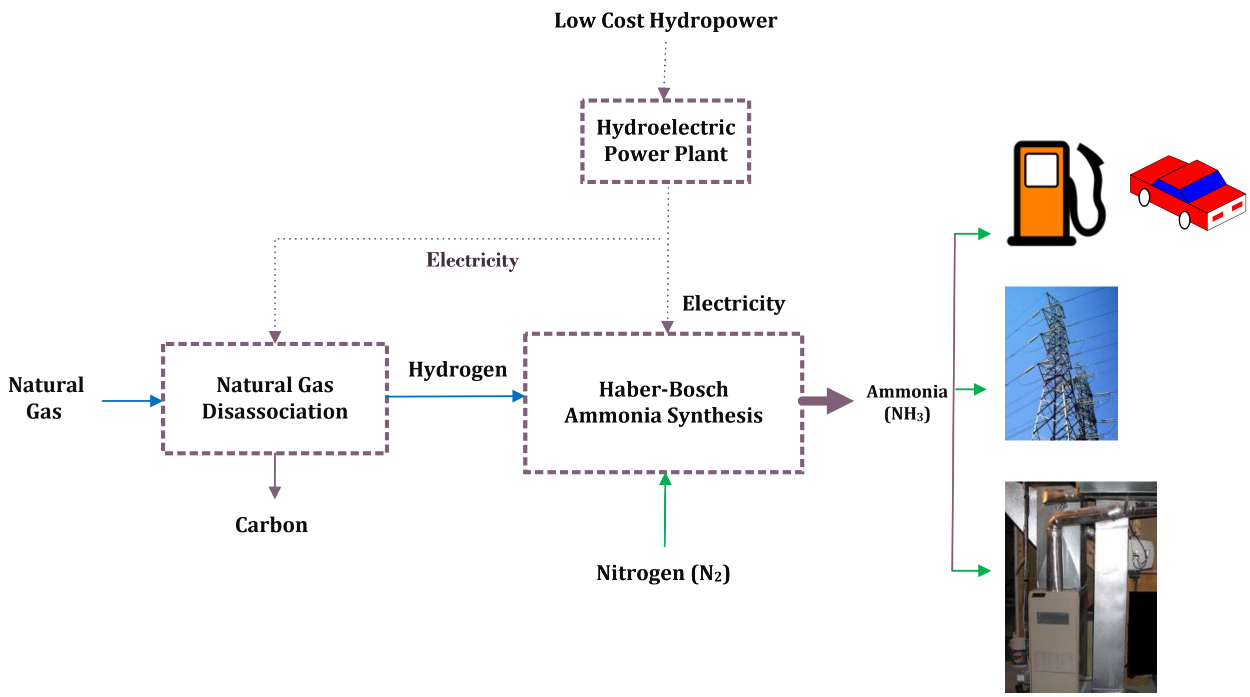

Fig. 4. Schematic diagram of ammonia production from low-cost hydropower and natural gas and alternative utilization options

The efficiency and CO_2 emissions from steam methane reforming, coal gasification and methane pyrolysis are comparatively shown in Table 2. Using CCS technology with steam methane reforming decreases the efficiency down to 54% which is quite similar to methane pyrolysis method.

For the microwave dissociation of hydrocarbons for ammonia production, it is seen that the microwave energy may be of sufficient power and duration to cause microwave depolymerization of the high molecular weight materials such as bitumen. Microwave energy is environmentally friendly since it has no harmful effect during hydrocarbon cracking process.

Table 2. Comparison of hydrogen production technologies from fossil-fuels

Process	**Methane steam reforming**	**Coal gasification**	**Methane pyrolysis**
Reaction Heat of reaction ($kJ/mol-H_2$)	$CH_4+2H_2O \rightarrow CO_2+ 4H_2$ 63.25	$Coal+2H_2O \rightarrow CO_2+ 2H_2$ 89.08	$CH_4 \rightarrow C + 2H_2$ 37.43
Energy efficiency in transformation (%)	74	60	55
Energy efficiency with CCS (%)	54	43	55
CO_2 emission ($mol-CO_2/mol-H_2$)	0.34	0.83	0.05
Carbon production ($mol-C/mol-H_2$)	0	0	0.5

The Haber-Bosch (which is the most common method for ammonia synthesis) process converts atmospheric nitrogen (N_2) to ammonia (NH_3) by a reaction with hydrogen (H_2) using a metal catalyst under high temperatures and pressures:

$N_2 + 3H_2 \rightarrow 2\ NH_3$ ($\Delta H = -92.4$ kJ/mol or $\Delta H = -5435$ kJ/kg)

2. Comparative Assessment

In order to reveal the attractiveness of fuel ammonia, it is compared with various fuels including natural gas in terms of cost and environmental impact.

2.1 Ammonia vs Conventional Fuels

The production processes of various fuels are compared in terms of environmental impact in this section.

Fig. 5 shows the comparison of ozone layer depletion values for various fuels. Ammonia has lowest ozone layer depletion even if it is produced from steam methane reforming and partial oxidation of heavy oil. However, hydrocarbon (methane) cracking has even lower ozone layer depletion impact. Similarly, production of natural gas from various locations yield higher ozone layer depletion values as seen in Fig. 6. Production of fuel ammonia yields lower acidification values compared to petrol and natural gas production as shown in Fig. 7.

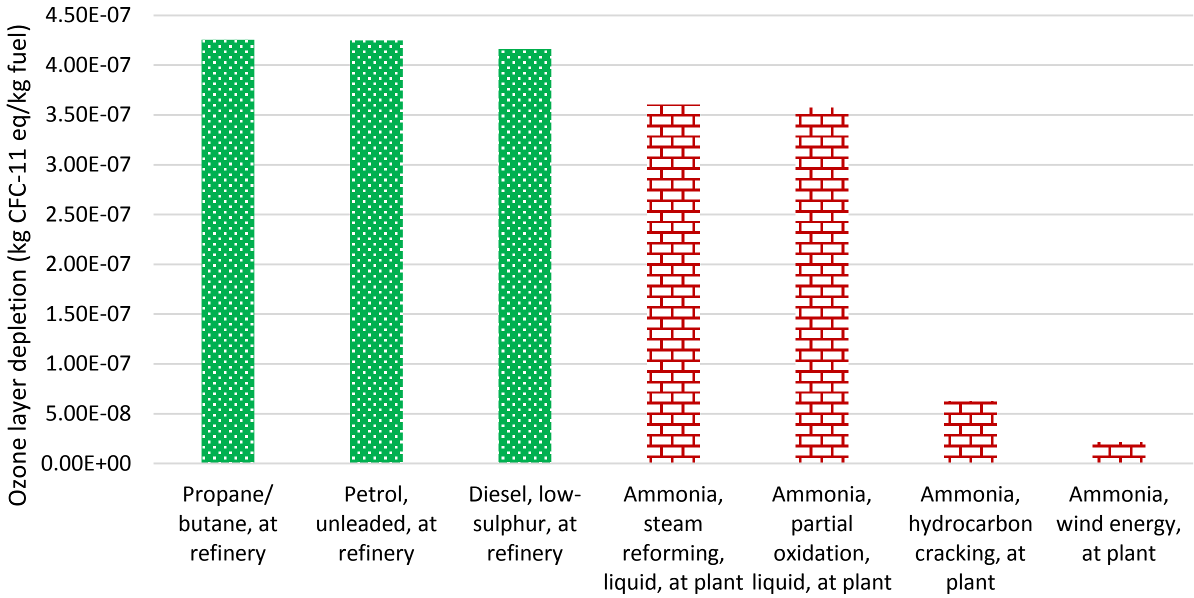

Fig. 5. Ozone layer depletion during productions of various fuels

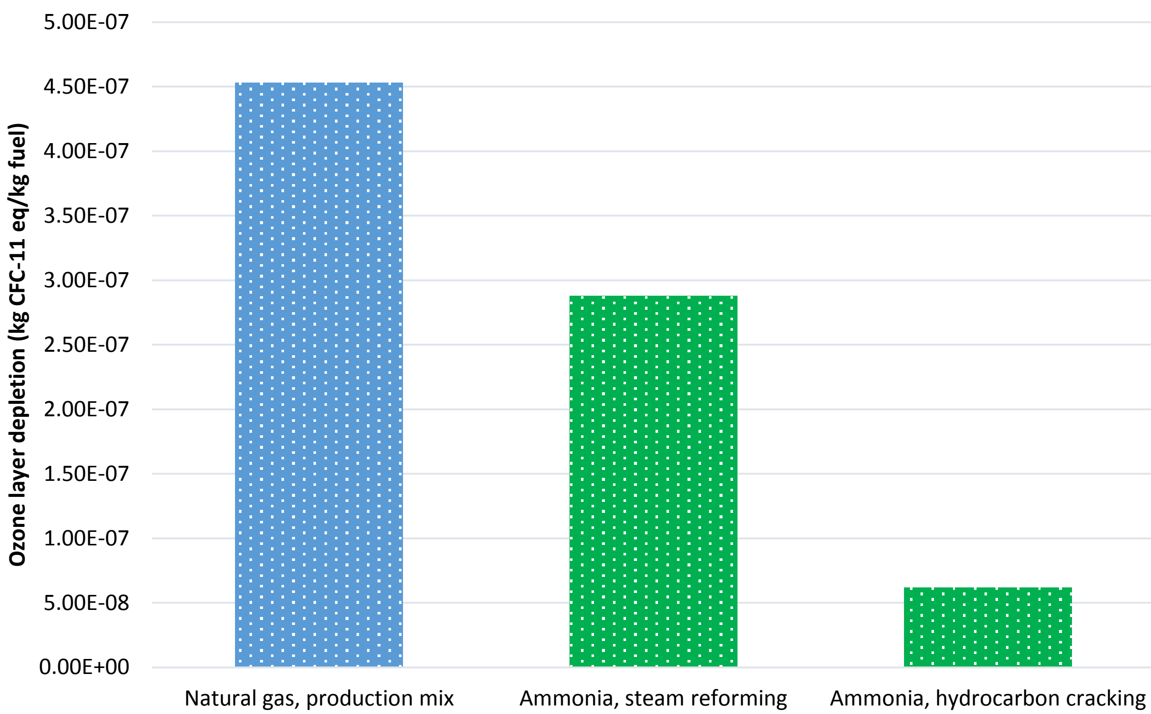

Fig. 6. Ozone depletion values during production of one kg of ammonia and natural gas

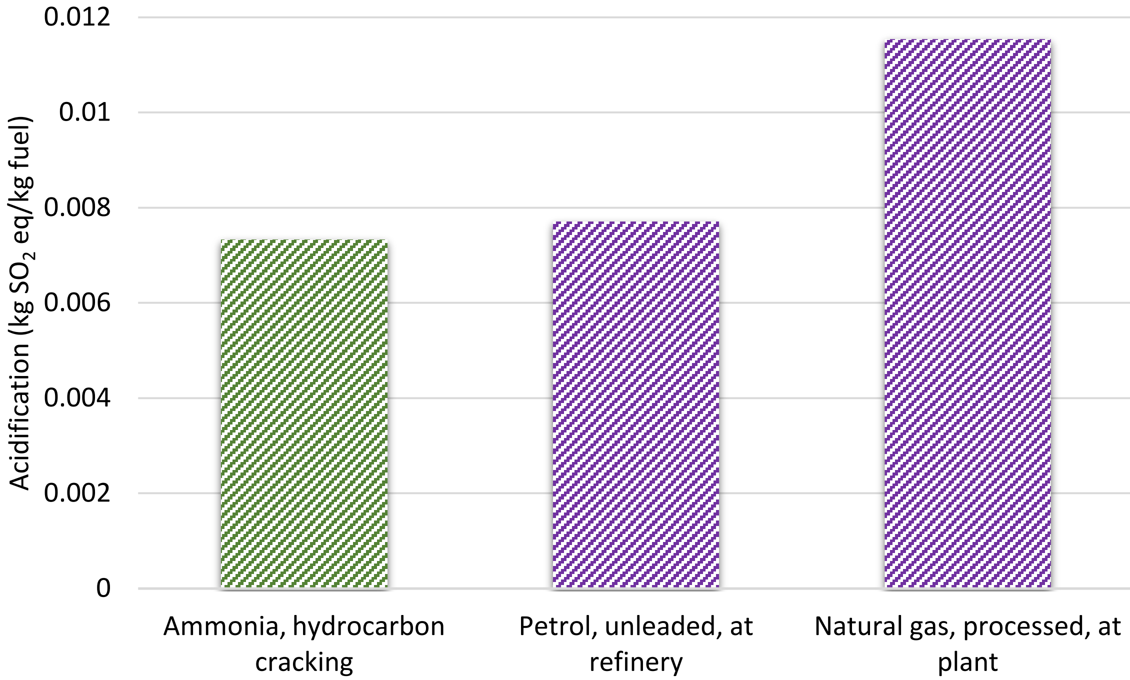

Fig. 7. Acidification values of ammonia, natural gas and petrol during one kg fuel production process

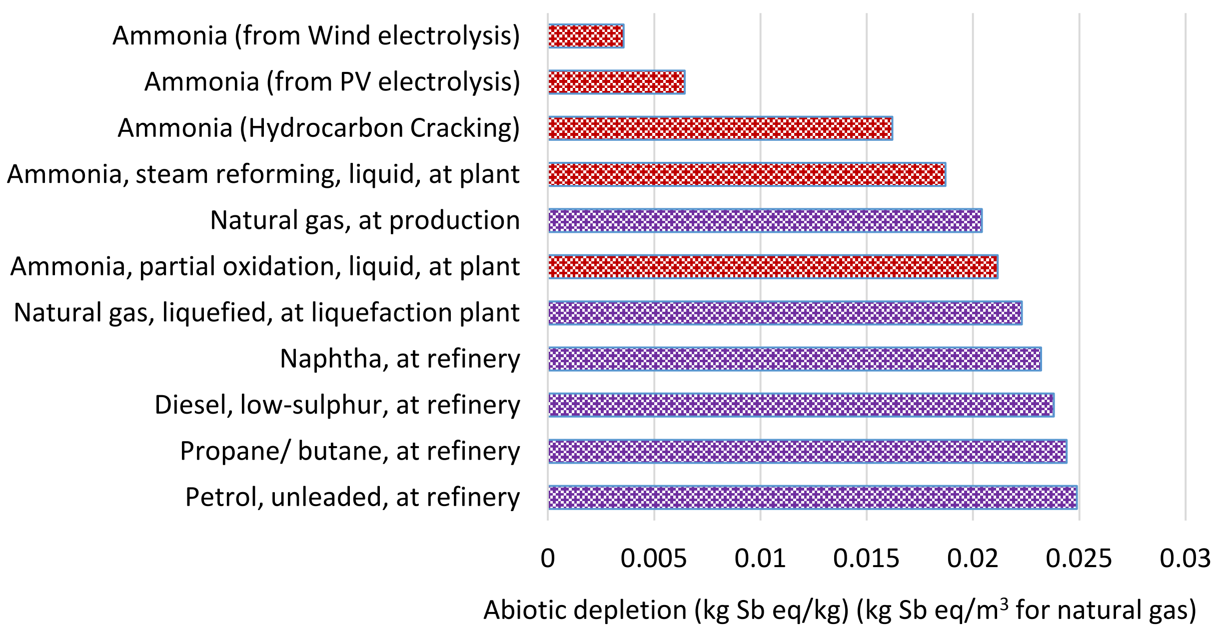

Fig. 8. Abiotic depletion values during production of various fuels including natural gas

Abiotic depletion is concerned mainly for 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 defined. As seen in Fig. 8, ammonia represents better performances.

2.2 Ammonia driven vehicle vs. Conventional vehicles

In this section, a comparison of ammonia fueled vehicles with other conventional fuels including natural gas is conducted to emphasize the cleaner and lower cost utilization pathway of ammonia.

The illustrative cost comparison of various fueled vehicles is shown in Fig. 9 and Fig. 10. Considering the current market prices of the fuels, ammonia is the lowest cost fuel corresponding to about 3.1 US$ in a 100 km driving range. This shows that ammonia is a promising transportation fuel in terms of cost. There is an advantage of by-product refrigeration which reduces the costs and maintenance during vehicle operation. Some additional advantages of ammonia are commercial availability and viability, global distribution network and easy handling experience. Ammonia is a cost effective fuel per unit energy stored onboard compared to methanol, CNG, hydrogen, gasoline and LPG as shown in Fig. 9.

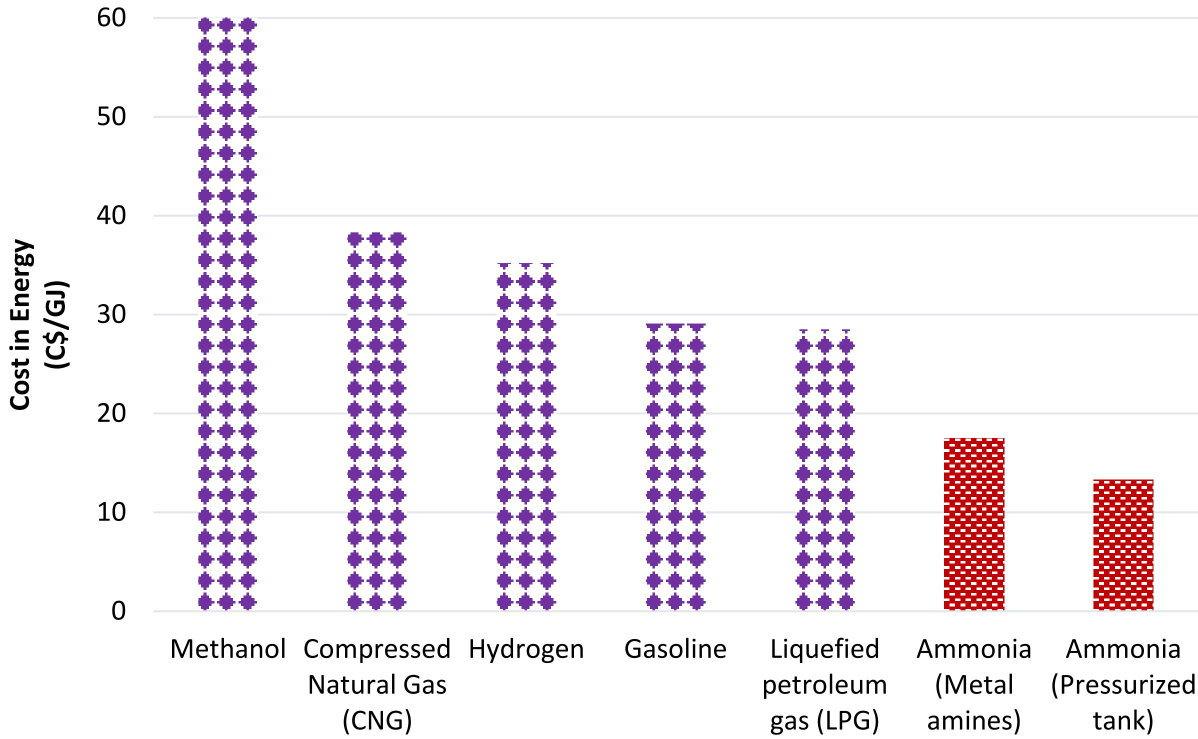

Fig. 9. Comparison of various vehicle fuels in terms of energy cost per gigajoule (Zamfirescu and Dincer, 2011)

The environmental impacts of the selected routes are also critical for the decision making. Impacts of the environment can be assessed using a life cycle assessment (LCA) approach which is principally a cradle to grave analysis method to examine environmental impacts of a system or process or product. LCA denotes a methodical set of processes for assembling and investigating the inputs and outputs of materials and energy, and the related environmental impacts, directly assignable to the product or service during the course of its life cycle (Bicer et al. 2016). Fig. 11 depicts the overall life cycle of various fueled vehicles. Here, it is also obvious that ammonia is the most environmentally benign option for the vehicles. The total greenhouse gas emissions are considerably lower than any other alternative fuels.

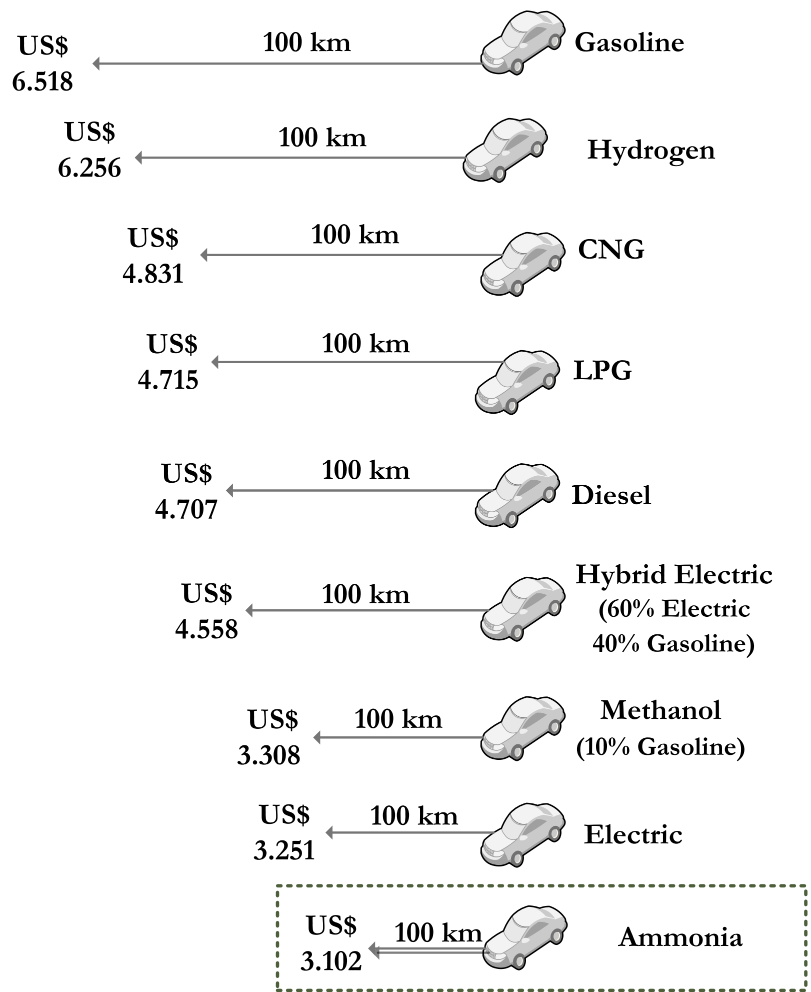

Fig. 10. Comparison of driving cost for various fueled vehicles

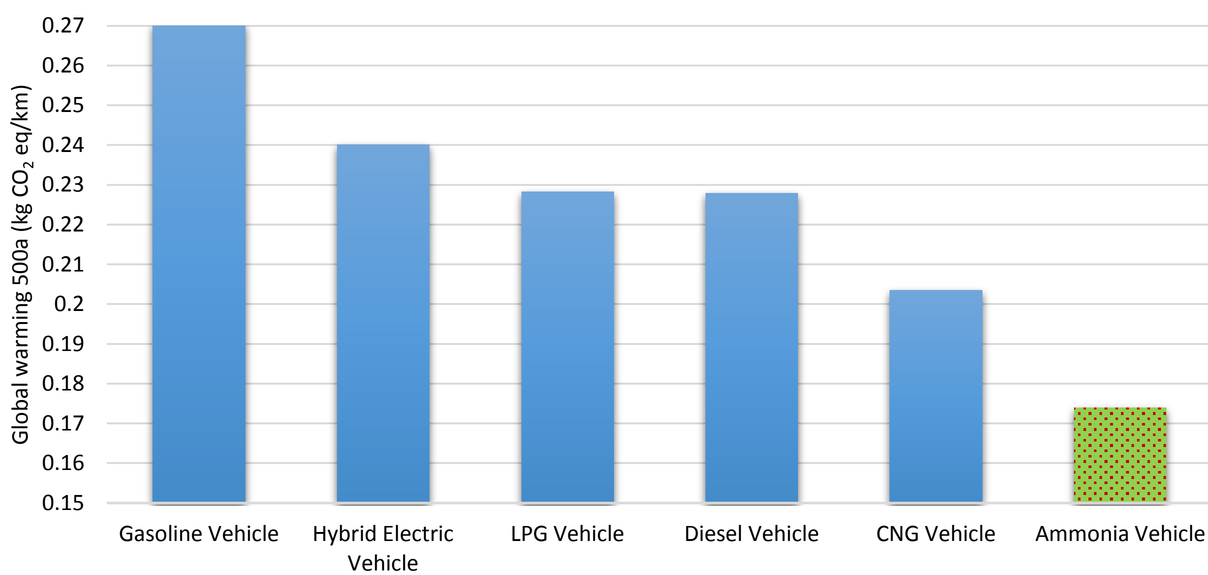

Fig. 11. Life cycle comparison of global warming results for various vehicles

Fig. 12 compares the global warming potential of ammonia driven vehicle where ammonia is either produced from solar energy or hydrocarbon cracking. Global warming potential of ammonia driven vehicle is similar for solar energy and fossil hydrocarbon based options. Hence, the utilization of ammonia in the transportation sector will certainly contribute to lessen global warming effect by using clean technologies even it is originated from fossil fuels. British Columbia, having significant amounts of natural gas resources, can compete with renewable resources if adequate and clean utilization pathways are used.

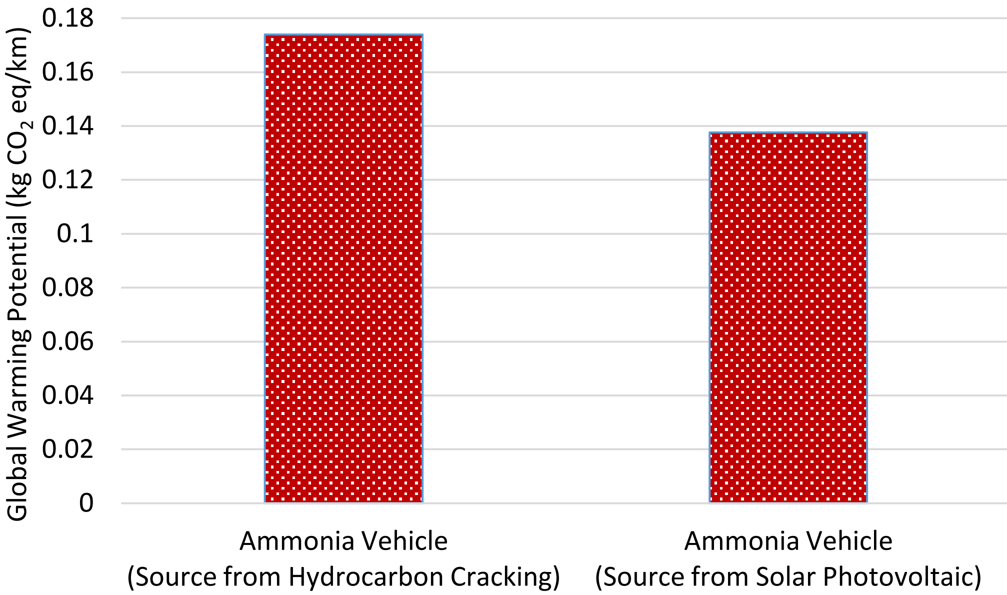

Fig. 12. Comparison of life cycle environmental impact of ammonia fueled vehicle from hydrocarbons and solar photovoltaics per km distance traveled

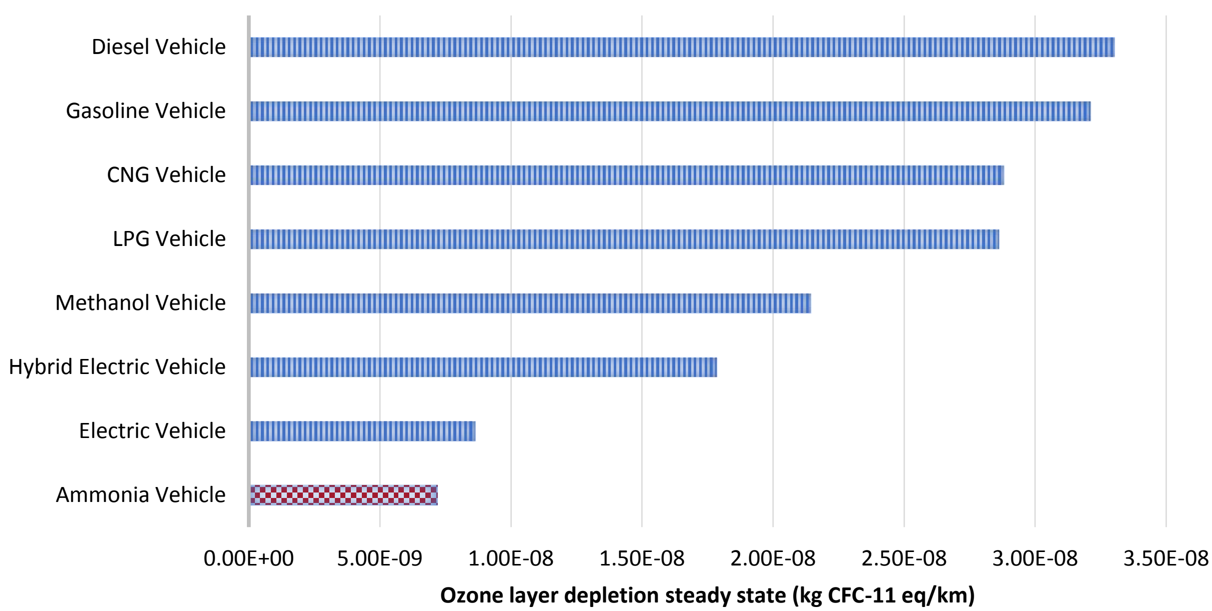

Fig. 13. Life cycle comparison of ozone layer depletion results for various vehicles

The depletion of ozone layer is one of the main reasons of environmental changes which is actually caused by carbon emissions to the atmosphere. Since diesel, gasoline, CNG and LPG fuels are fossil based and have huge amount of carbon substance, they have higher ozone layer depletion values. The highest is equal to 3.3×10^{-8} kg CFC-11 eq. per km for diesel vehicle as Fig. 13 represents. The lowest contributions are from ammonia vehicle corresponding to 7.19×10^{-9} kg CFC-11 eq/km. Because there is no direct CO_2 emission during operation of ammonia vehicle.

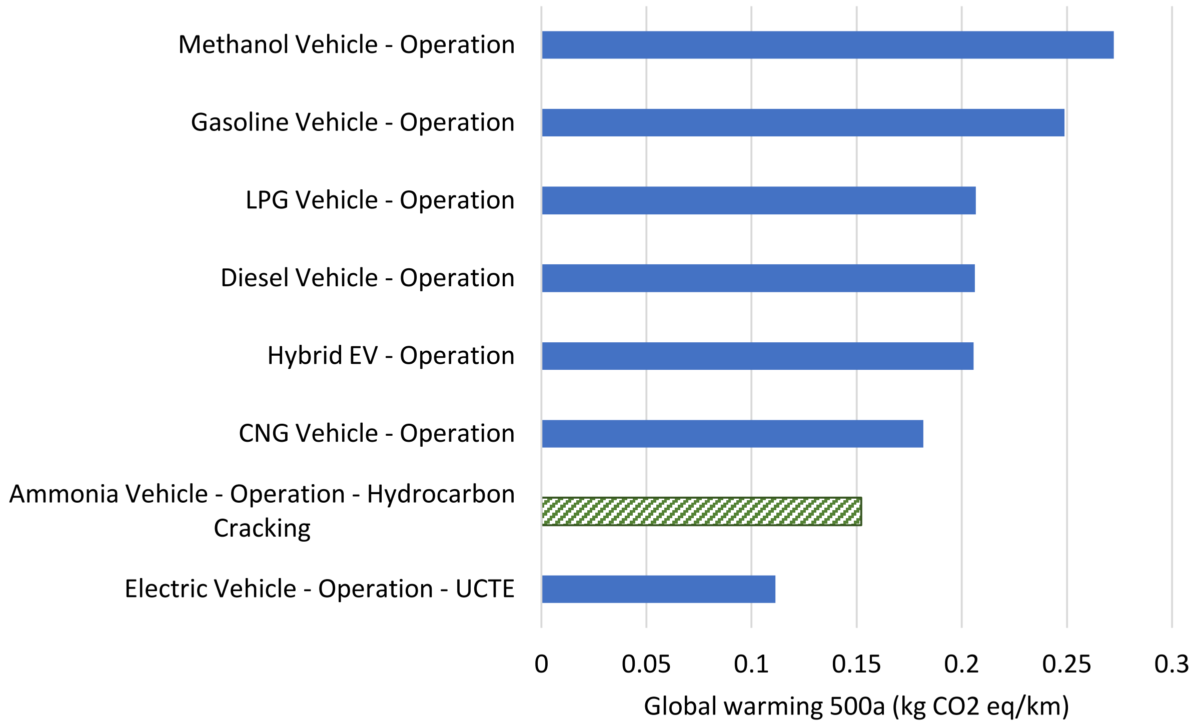

Fig. 14. Life cycle comparison of global warming results for operation only of various vehicles

Besides manufacturing and disposal of the vehicles, operation process is the fundamental part for the vehicle life cycle. As seen in Fig. 14, ammonia driven vehicles is the second environmentally benign option after electric vehicles during the operation.

Fig. 15 illustrates the single score results of ammonia driven vehicles from various resources. Overall wind energy based option yields lower environmental impact, however, hydrocarbon cracking and solar PV option have similar impact factors emphasizing the attractiveness of hydrocarbon utilization.

On the other hand, ozone layer depletion value of ammonia vehicles where ammonia comes from PV electrolysis has the highest value. It is noted that hydrocarbon cracking based ammonia driven vehicle yields similar impacts with wind and lower impacts than solar based option as Fig. 16 shows.

In Fig. 17, the green bars on the left represent the number of times ammonia vehicle had a lower environmental impact than CNG vehicle. For instance, it shows that in 100% of the cases the climate change impact score is lower for ammonia. In about 20% of the cases, the fossil fuels category is lower in CNG vehicle. Overall, it is noted that ammonia driven vehicle is more environmentally friendly compared to CNG vehicle.

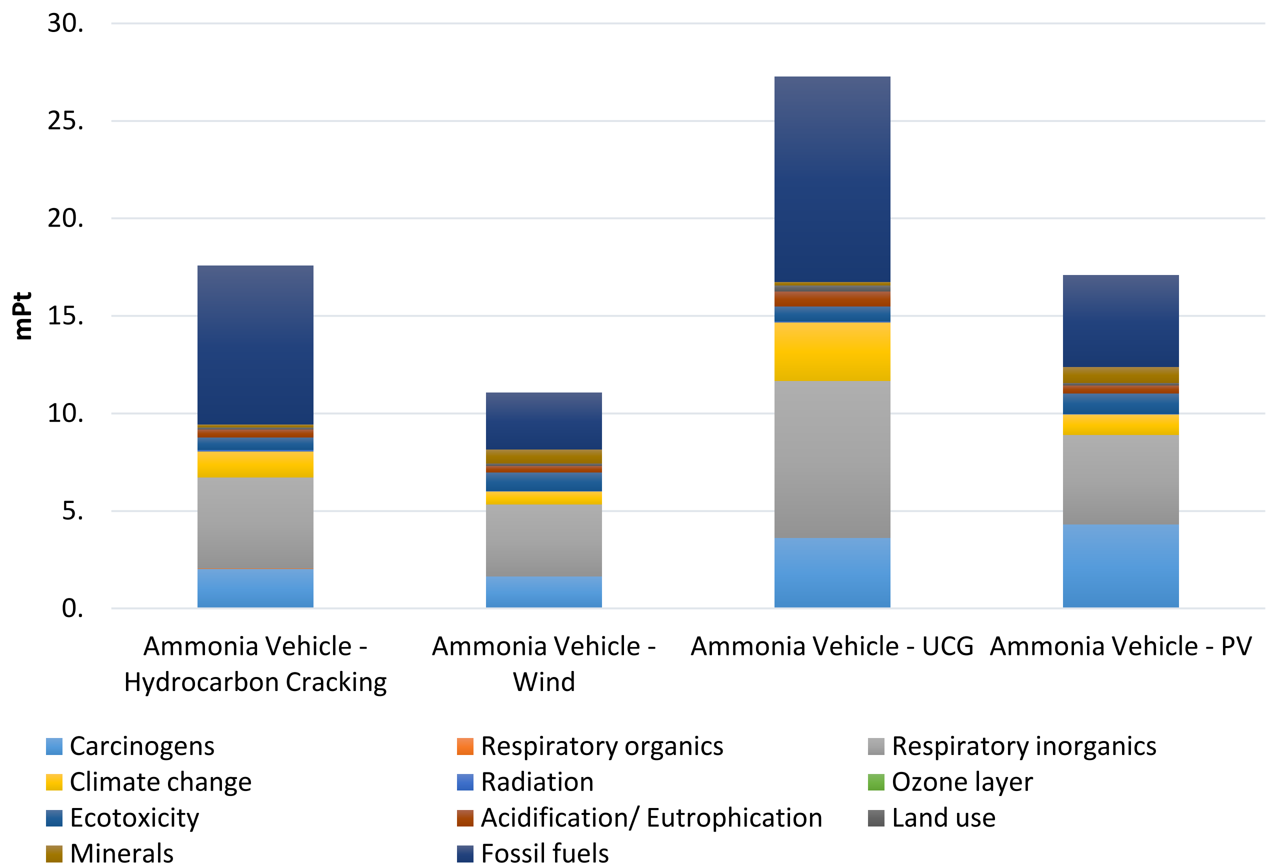

Fig. 15. Singe score comparison of various source ammonia vehicles

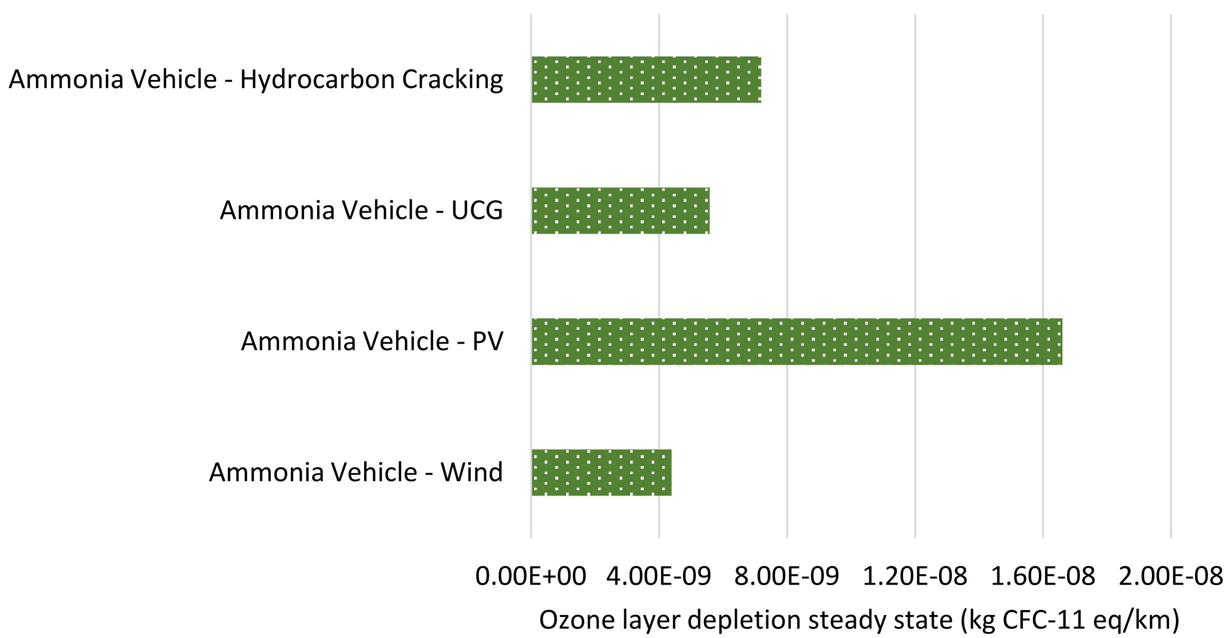

Fig. 16. Ozone layer depletion comparison of various source ammonia vehicles

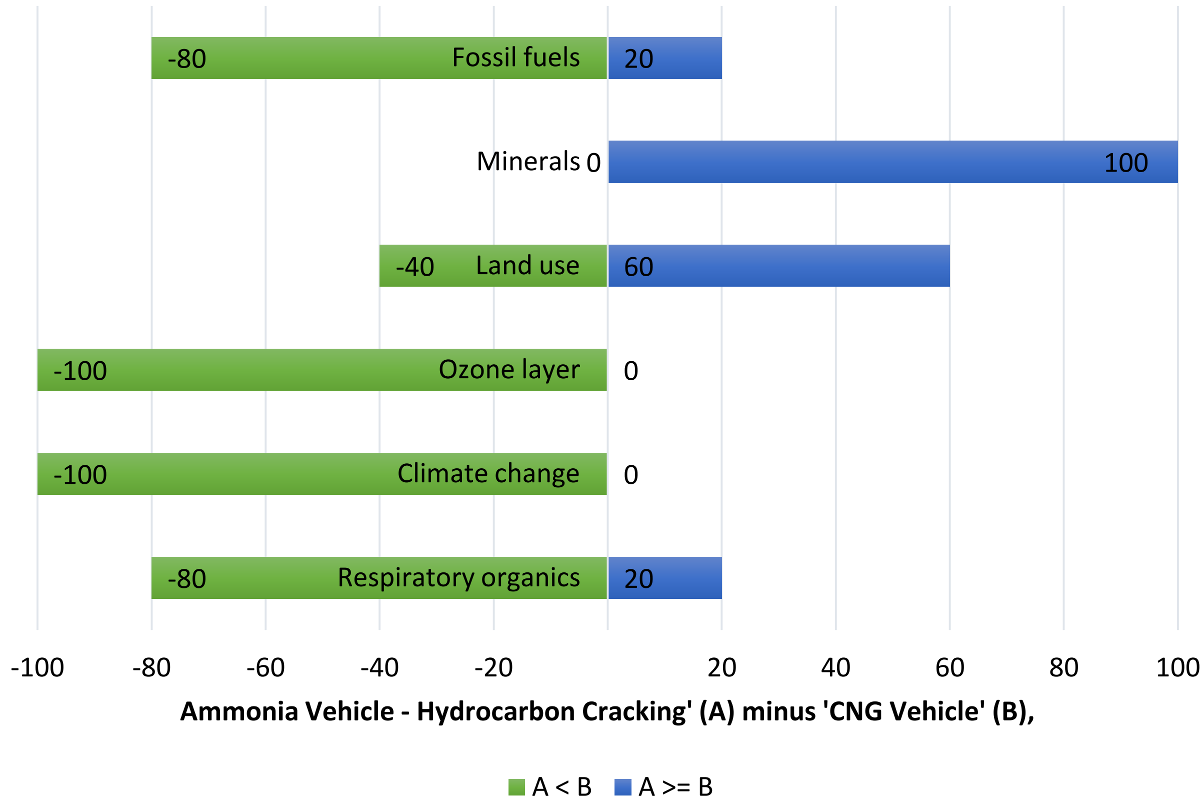

Fig. 17. Monte-Carlo simulation results of characterized LCA comparison between ammonia and CNG vehicle

2.3. Production of ammonia

There are multiple pathways for ammonia production. In this section, they are comparatively assessed and presented. Fig. 18 shows the comparative cost of ammonia production from renewable and conventional resources. Currently, steam methane reforming is the dominant method of production. However, as seen in the figure, hydrocarbon dissociation yields lower costs than low cost hydropower option and steam methane reforming method. Furthermore, hydrocarbon dissociation also produces carbon black which is a commercial commodity in the market. For example, per each kg of ammonia produced, about 0.5 kg of carbon black can be obtained from methane dissociation. If the price of carbon black is assumed to be 1 US$/kg in the market, the cost of ammonia for the hydrocarbon dissociation scenario decreases down to 0.17 US$/kg.

Fig. 19 shows the acidification potential (AP) for the selected routes. Acidifying substances causes a wide range of impacts on soil, groundwater, surface water, organisms, ecosystems and materials. It is mainly caused by hard coal usage in the electricity grid mixture. Fig. 20 shows the ozone layer depletion (ODP) potential of the routes. Due to stratospheric ozone depletion, a bigger portion of UV-B radiation hits the world surface. It may have damaging properties upon human health, animal health, terrestrial and aquatic ecosystems, biochemical cycles and on materials. Hydrocarbon route has the lowest ODP value whereas wind has the highest since it is mainly caused by the transport of natural gas which is used in the power plants where the electricity is supplied to wind turbine production. It is important to note that although hydrocarbon route is a fossil fuel based option, the environmental impacts are not that bad because of the dissociation method used in the analyses. Instead of reforming via steam, hydrocarbons are decomposed to carbon black and hydrogen yielding lower GHG emissions.

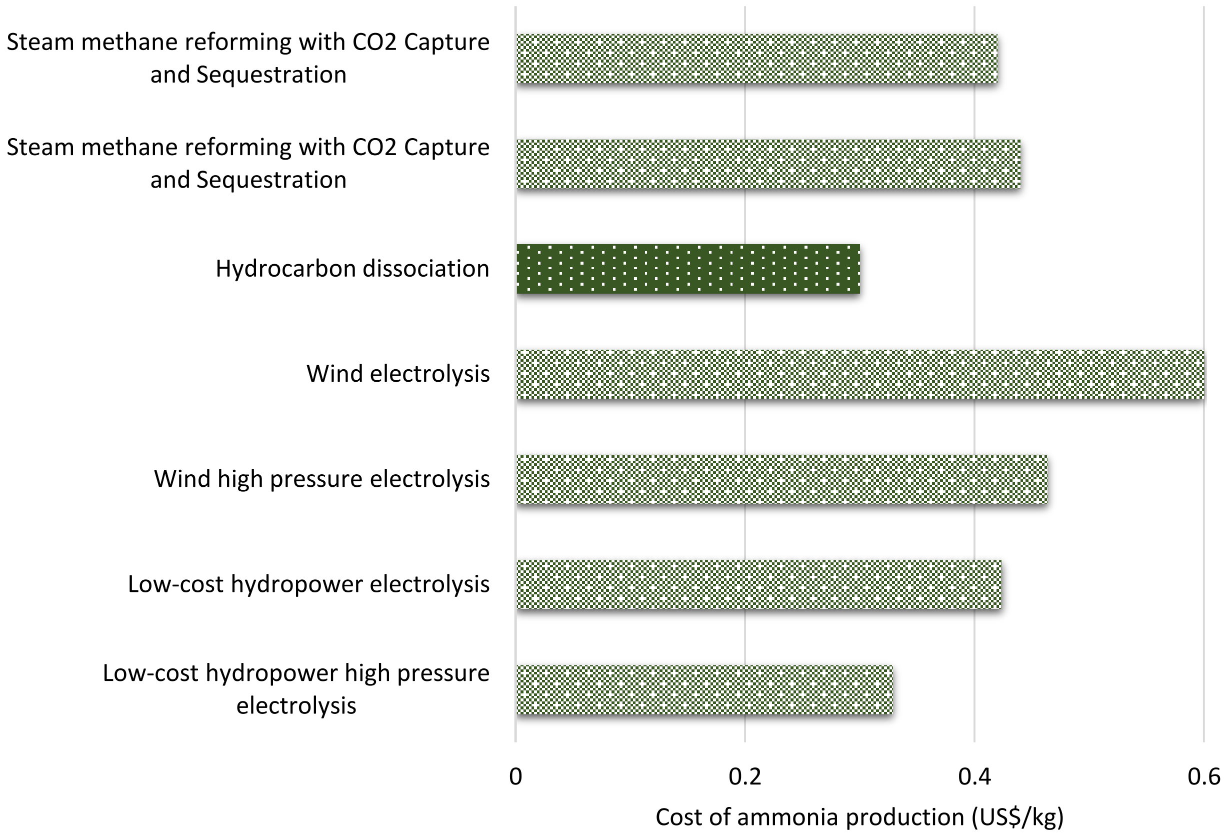

Fig 18. Comparison of cost of production for ammonia using various routes

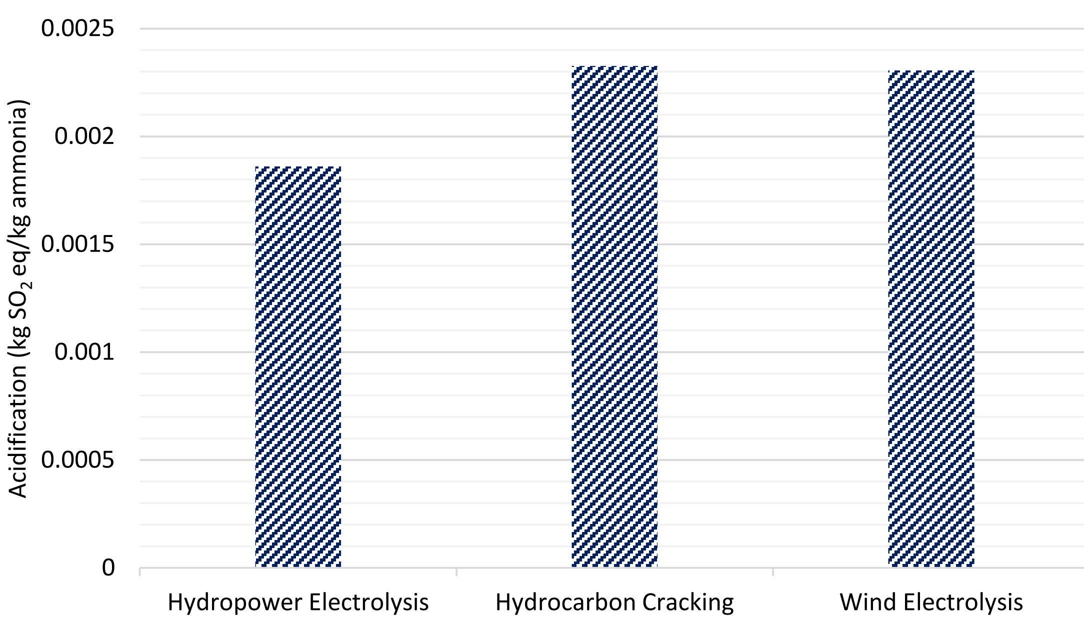

Fig. 19. Acidification impact comparison of selected ammonia routes

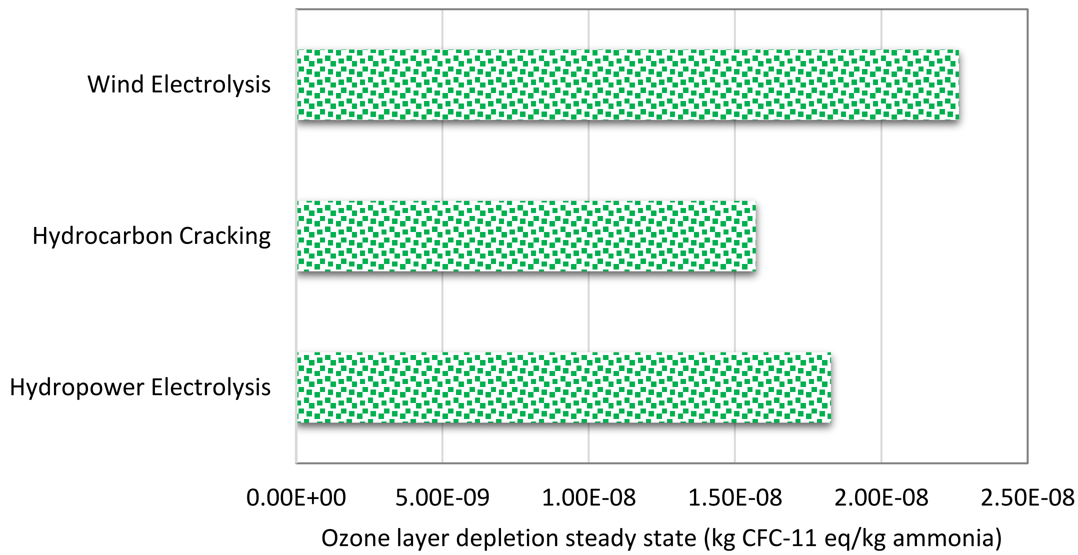

Fig. 20. Ozone layer depletion impact comparison of selected ammonia routes

Fig. 21 compares the total greenhouse gas emissions during production of 1 MJ energy from various resources including gasoline, LPG, diesel, natural gas and ammonia. Production of 1 MJ energy from ammonia has lower emissions than gasoline, LPG, diesel and natural gas.

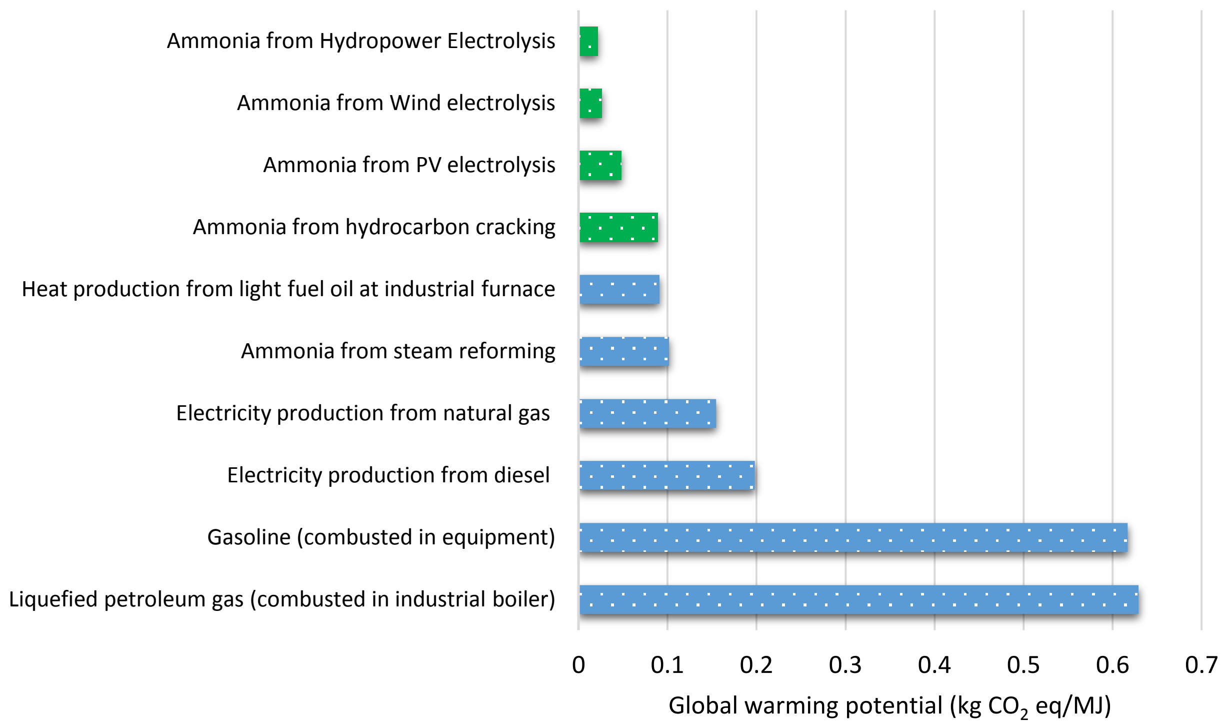

Fig. 21. Comparison of global warming potential of 1 MJ energy production from various resources

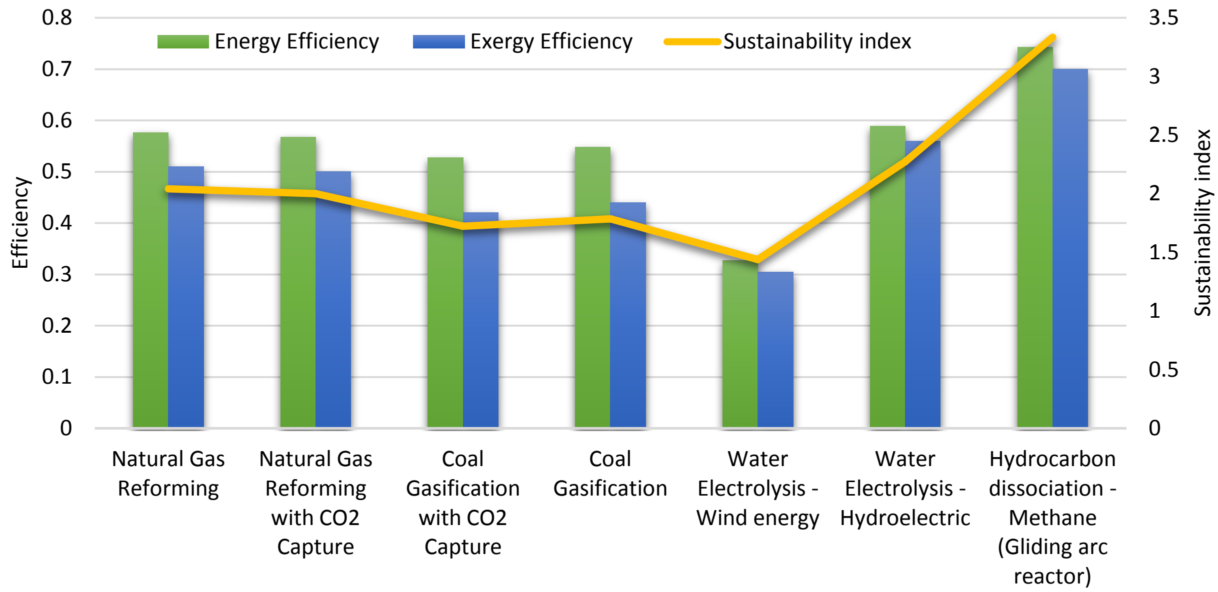

Fig. 22. Efficiency and sustainability comparison of various ammonia production routes

Although hydrocarbon (methane) dissociation is a recently developing method, it has quite higher efficiencies compatible levels with mature natural gas reforming option as shown in Fig. 22. Enhanced energy and exergy efficiency of hydrocarbon dissociation brings higher sustainability values enabling cleaner utilization of natural gas.

3. Closing Remarks

Utilization of hydrocarbons in an environmentally friendly manner becomes more significant day by day. Dissociation of hydrocarbons such as methane is a promising option especially for British Columbia. Based on the extensive literature review and assessments, the following concluding remarks are noted.

- Hydrocarbons can be used as a source of hydrogen which is required for ammonia synthesis. There are various alternative pathways for hydrogen production from hydrocarbons such as thermal, non-thermal, plasma routes.
- Methane decomposition reaction is moderately endothermic process. The energy requirement per mole of hydrogen produced is considerably less than that for the steam reforming process.
- Hydrogen via thermo-catalytic dissociation of hydrocarbons represents an alternative solution. It is accompanied by the formation of carbon deposits. Methane can be thermally or thermocatalytically decomposed into carbon and hydrogen without CO or CO_2 production.
- It can be estimated that the electric energy supply needed for the cracking operation varies between 4 and 7 kWh per kg of carbon produced or between 1 and 1.9 kWh per normal cubic meter of hydrogen produced.
- Gliding arc discharge reactor is one of the highest efficient route for methane conversion which was experimentally tested by many researchers.
- H_2 production cost that can be expected from industrial methane cracking could be of the order of 1.5 $/kg and NH_3 in the range of 0.3-0.5 $/kg.

- The microwave energy can be of sufficient power and duration to cause microwave depolymerization of the high molecular weight materials such as bitumen.
- For oil sands or extremely high viscosity reservoirs, where the temperature effect on viscosity is significant, electromagnetic heating could be used as a preheating purposes. Because lower frequency waves carry less energy, heating times are considerably longer compared to the higher energy microwaves.
- The current ammonia retail prices continue to decrease by low natural gas prices. Current retail price is about 550 US$/ton. However, ammonia price is strictly dependent on natural gas price which can be eliminated if oil sand bitumen is utilized.
- Although natural gas dissociation route is a fossil fuel based process, the technology is clean and environmentally friendly close to renewable resources in some environmental impact categories.

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