SPECIFIC REPORT

Ammonia as a Potential Solution for Alberta

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Abstract

Ammonia is projected to be a potential hydrogen carrier 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 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 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. The capability to convert a liquid at adequate pressure permits ammonia to store more hydrogen per unit volume than compressed hydrogen/cryogenic liquid hydrogen. Besides having a significant advantages in storing and transporting hydrogen, ammonia may also be burned directly in internal combustion engines. Compared to gasoline vehicles, ammonia-fueled vehicles do not produce direct CO_2 emission during operation.

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.

Introduction

The decarbonisation of fossil fuels, particularly, oil sand bitumen and 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.

Alberta denotes one of the safest and major sources of crude oil in the world. As demand for oil products is increasing, Alberta oil sand resources present an important alternative to support the growth of product demand and it will decrease external need for the North America. At the moment, it is considered that Alberta has third biggest oil reserves in the world.

Microwave energy is an alternative type of energy which can be used in oil sand separation. Many of the inorganic particles in processed oil sands carry a charge, and could be influenced by electromagnetic radiation. They are thrilled at an altered rate than the water and bitumen when irradiated, making a temperature gradient between the different components of the oil sands. The surfactants and other forces cannot cope with this gradient and the solids are able to break free. Since all oil sands are dissimilar, a single frequency or power of microwaves are not available which functions best for all.

There have been already some attempts for dissociation of bitumen using microwave energy. Pierre et al. [1] used a 915 MHz microwave to separate a 570 g sample of oil sands. This sample was exposed for 5 min at 500W and extended a last temperature of 315°C. This resulted in numerous layers comprising a bottom layer of sand with an asphaltene-like material on top. A second, noticeably bigger specimen with a volume of about 20 L was exposed for 9 min at 1500W at the same frequency. It got a temperature of 142°C where it exhibited three distinct layers. The bottom layer was typically sand, but also included other solids. The second layer contained a yellowish solution, accounting for all the water and other impurities in the oil sand. The top layer was black, viscous oil. Bosisio et al. [2] considered microwave-assisted extraction of oil sands. They conducted oil sand extraction experiments under inert atmosphere in a quartz reactor which was located in a rectangular microwave guide (WR 284 wave guide) built-in with a coupling iris and modifiable short circuit. Instance microwave power of 100W at 2450 MHz frequency was realized to the oil sands samples and the different phases of reaction were perceived. The duration of first was 10 to 15s and second-third step were 15s to 15 min. Microwave radiation of oil sands created a crude oil and also small quantities of gaseous yields. Therefore, electromagnetic heating also proved to increase yields of crude oil from 70% to 86%. Lately, Global Research Corporation technologies declared a method using over 8,700 RF microwave frequencies essential to hydrocarbon elements. About 1.2 gal of diesel fuel was extracted from a tire after microwave radiation under vacuum at different frequencies. The company requested to extract oil and gas from diverse feedstocks by microwave radiation such as oil sands, oil shale, used plastics, or rubber with little or no additional processing. Initial testing results formed great amounts of hydrogen and methane gases without CO or CO_2 contaminants [3, 4]. Samples of Lloydminster oil sands (oil–water–solids ratio of 19:40:41) considered principally stubborn to separation were tested with exposure to adjustable frequency microwaves [5]. The tests were able to avoid the FCC regulations because of distinct apparatus to comprise the electromagnetic waves. The aim was to explore what microwave frequency is best for this type of oil sands. All samples separated into a liquid upper layer and a mostly solid lower layer. The degree of separation was calculated by evaluating the oil content of the lower layer. The lower layer of the control specimen, which was not irradiated, had 27% oil content by weight. Tests were achieved by changing frequency and exposure time. Most of the samples presented marginally lower oil content. The best result occurred when the sample was irradiated for a duration of 10 min at 6400±100 MHz, where the lower layer only had 19% oil content. It was described microwave assisted extraction to recover hydrocarbon substances from oil shale, oil sands and lignite in the U.S. Patent 4.419.214 [6]. The patent describes how oil sand, oil shale rock and lignite samples were irradiated in a pressure vessel with gaseous or liquefied carbon dioxide and other gaseous or vapor hydrocarbon solvents. For example, oil sand was taken into a microwave feeder pipe and irradiated at 5.8 GHz frequency. Further, BTX (benzene-toluenexylene-ethylbenzene) was pumped through the sand. The extraction solution contained green oil on the top and bitumen was obtained at the bottom. In another example, crushed oil shale rock was irradiated at 915 MHz frequency. After radiation, carbon tetrachloride was impelled to extract kerogen and the projected isolated kerogen was 65% of initial organic content of the rock. Dumbaugh et al. [7] specified that oil sands and oil shale samples irradiated to microwaves produced the required heat to dissociate bitumen components to produce a crude oil and distilled kerogen. A laboratory microwave oven was utilized to test oil sand samples from Athabasca and oil shale specimens from Green River and Sunnyside. The authors found that a 128 g sample of oil sand separated into its components when irradiated at 800W for 10 min, followed by 1500W for 15 min.

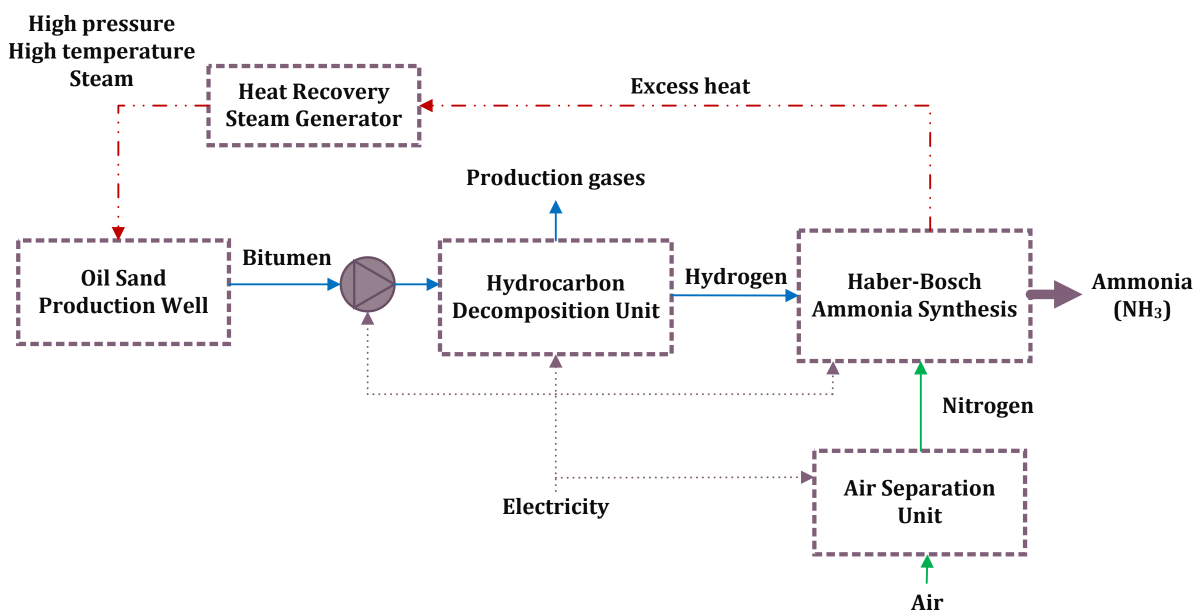

Fig. 1. Schematic diagram of oil sand to ammonia plant

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. Optimized ammonia synthesis using the excess heat in Haber-Bosch (which is the most common method for ammonia production) ammonia plant for oil sand bitumen extraction which is used for hydrogen production via microwave dissociation process is possible as shown in Fig. 1.

The Haber-Bosch 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)

The excess heat in the Haber-Bosch reactor can be utilized via heat recovery steam generator (HRSG). The produced steam is injected underground to extract bitumen using a specific pump arrangement for high dense liquids. Application of microwave energy can yield production gases where a portion is hydrogen. The generated hydrogen can be utilized in a conventional Haber-Bosch process for ammonia synthesis.

The ammonia synthesis via Haber-Bosch process releases approximately 2.7 GJ/tonne NH_3 heat. This is equivalent to about 8% of the energy input for the entire process. It means that heat dissipation from Haber-Bosch ammonia process is about 2700 kJ/kg ammonia. When 300 tonne/day ammonia is produced, the Haber-Bosch reactor releases 9375 kW heat. A small temperature approach (about 10–20°C) along the low temperature heat exchanger is possible and then a substantial (90–95 %) part of the reaction heat could be utilized.

Presumably 50% of the reaction heat is recovered. In this case, the excess heat for a 300 ton/day capacity ammonia production plants is about 9,375 kW. In the previous studies for Alberta bitumen extraction [8, 9], it was shown that in order to extract about 0.15 m^3/s bitumen via SAGD based process, the required energy input to the production well is approximately 15,600 kW. Bitumen extraction requires continuous production of high temperature high pressure steam. The required pressure of the steam being sent to SAGD (steam assisted gravity drainage) oil sand plant is about 1000 kPa and the temperature is about 380°C. Including the pressurization and evaporation of water, the total required power is about 18,000 kW. This amount of power can be recovered from approximately 600 tonne/day ammonia production plant. Hence, a suitable capacity ammonia production plant can be integrated for bitumen extraction and a valuable commodity, ammonia, can be produced from hydrocarbons.

1. Comparative Assessment

The illustrative cost comparison of various fueled vehicles is shown in Fig. 2. 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. In addition, Fig. 3 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.

The environmental impacts of the selected ammonia 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.

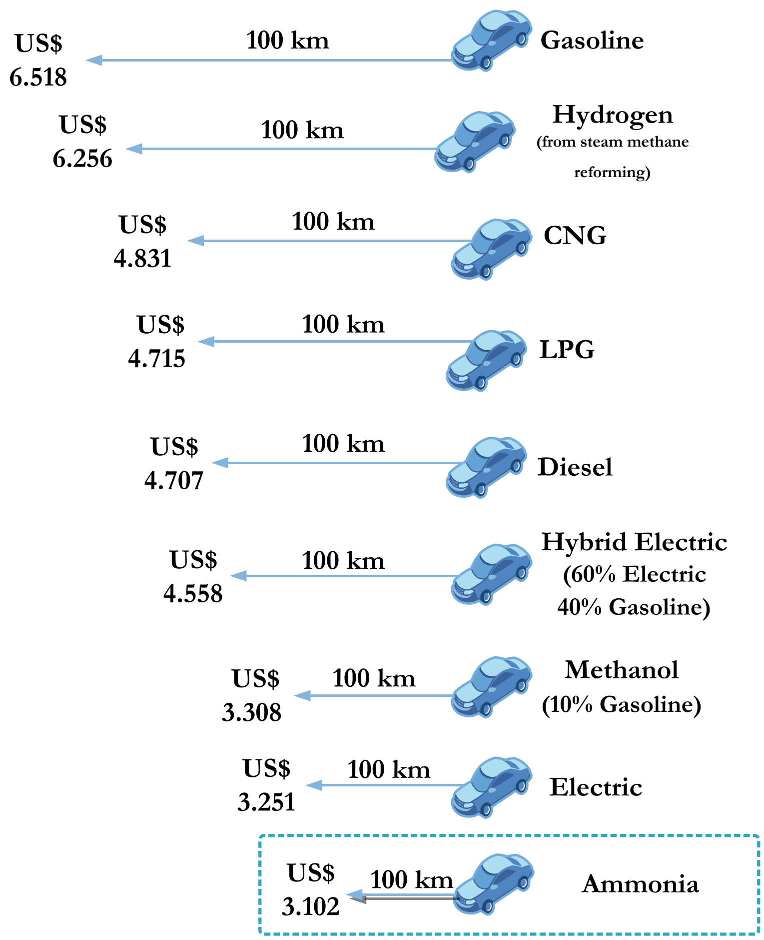

Fig. 2. Comparison of driving cost for various fueled vehicles

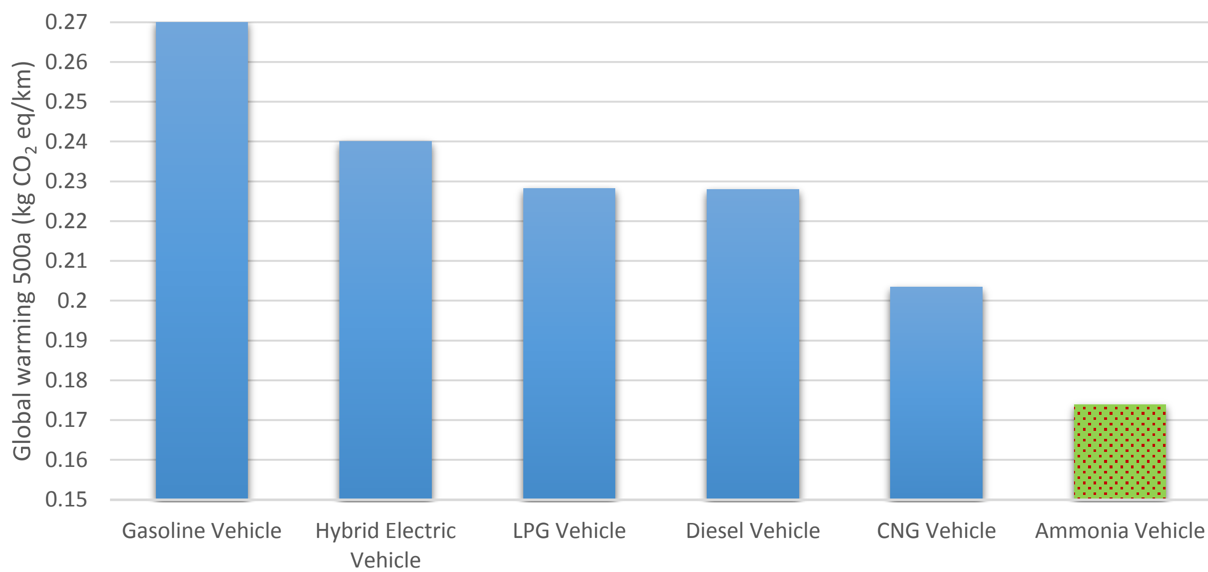

Fig. 3. Life cycle comparison of global warming results for various vehicles

Fig. 4 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. Alberta, having significant amounts of hydrocarbon resources, can compete with renewable resources if adequate and clean utilization pathways are used.

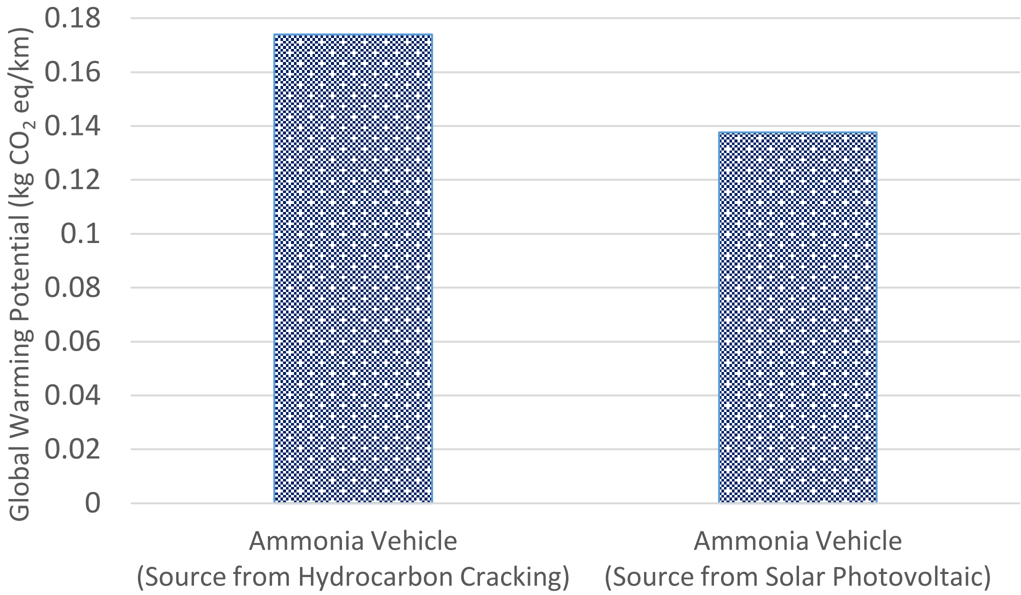

Fig. 4. Comparison of life cycle environmental impact of ammonia fueled vehicle from hydrocarbons and solar photovoltaics per km distance traveled

Fig. 5 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.

Fig. 6 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.

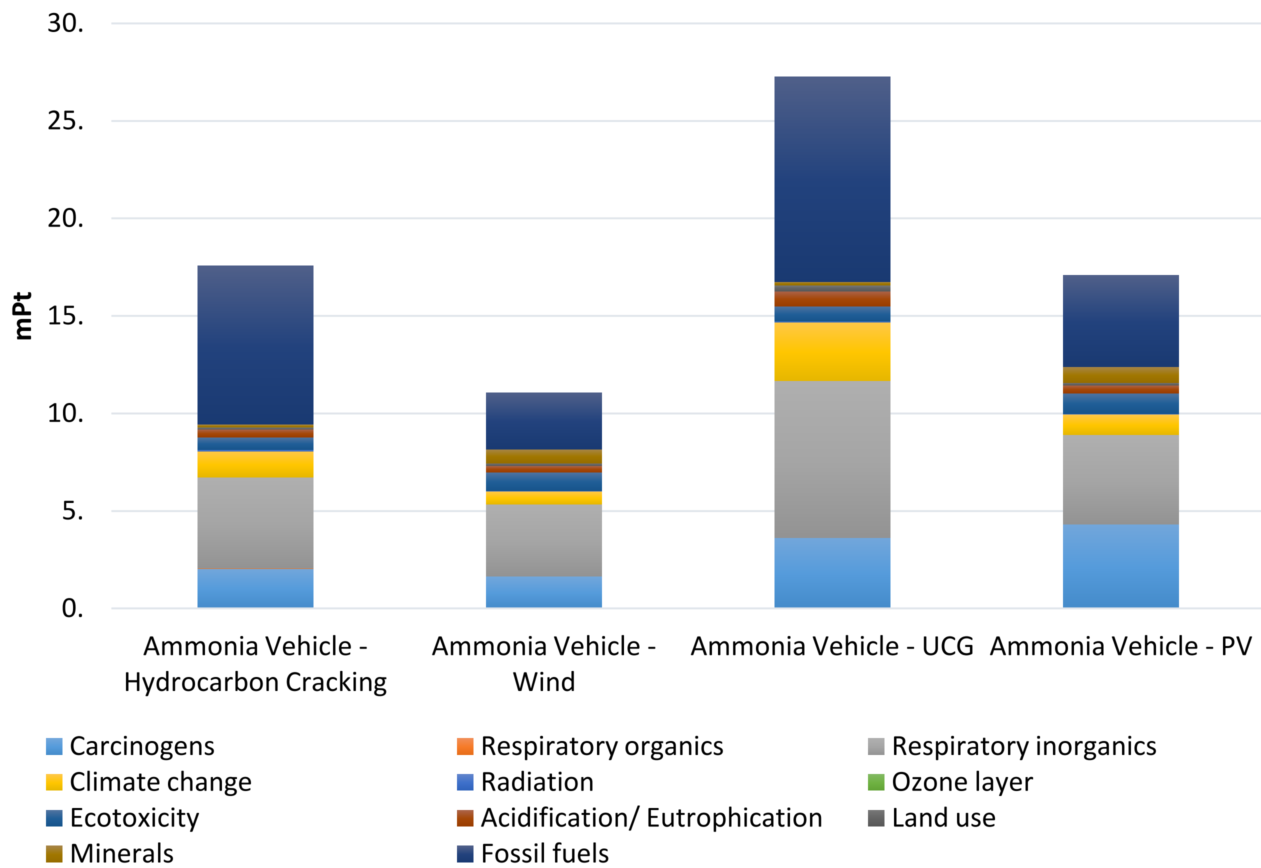

Fig. 5. Singe score comparison of various source ammonia vehicles

Fig. 7 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.

The eutrophication category reflects the impacts of to excessive levels of macro-nutrients in the environment caused by emissions of nutrients to air, water and soil. As shown in Fig. 8, the values are close to each other corresponding to 0.0012 kg PO_4 eq/kg ammonia for hydropower route.

Fig. 9 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.

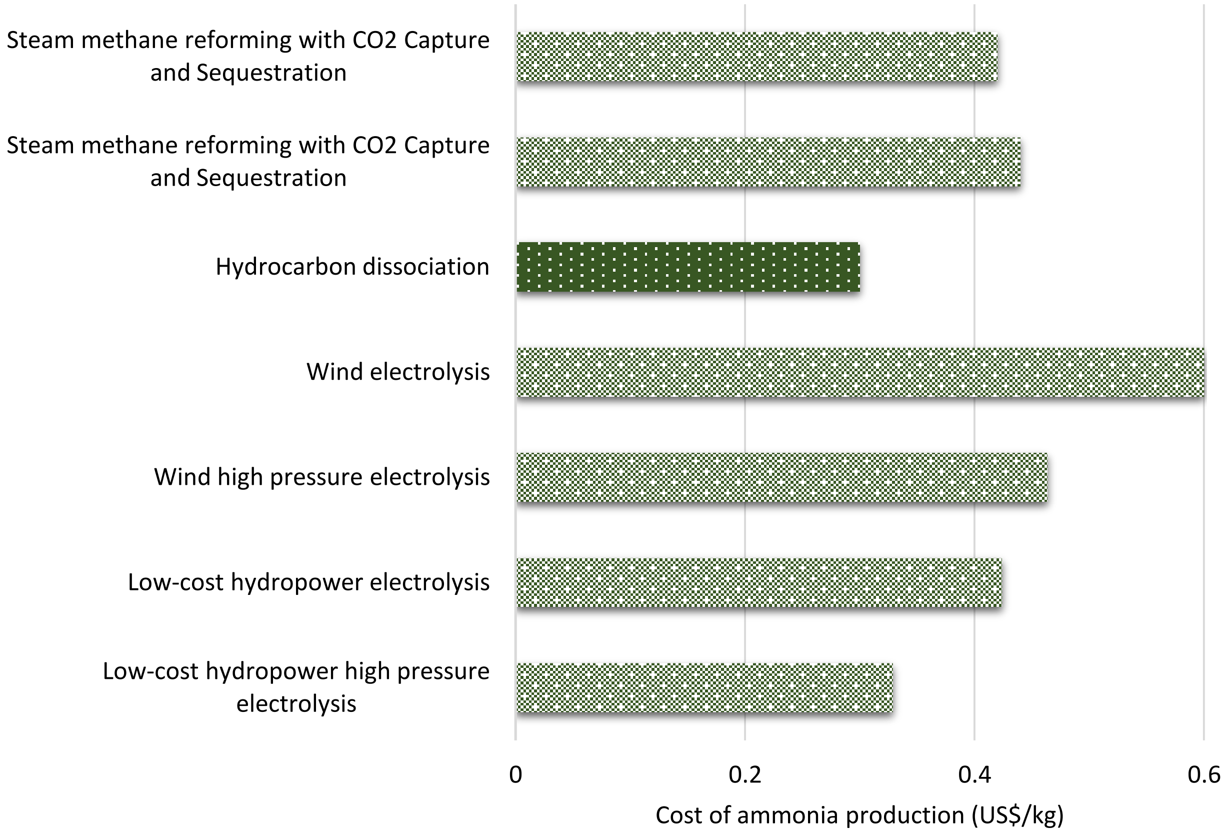

Fig 6. Comparison of cost of production for ammonia using various routes

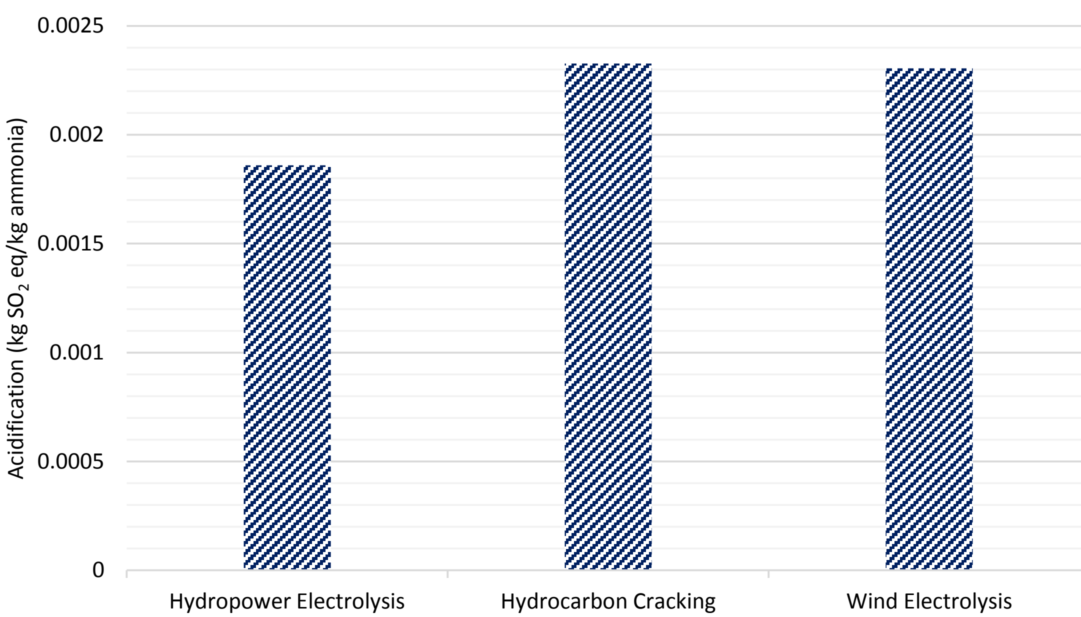

Fig. 7. Acidification impact comparison of selected ammonia routes

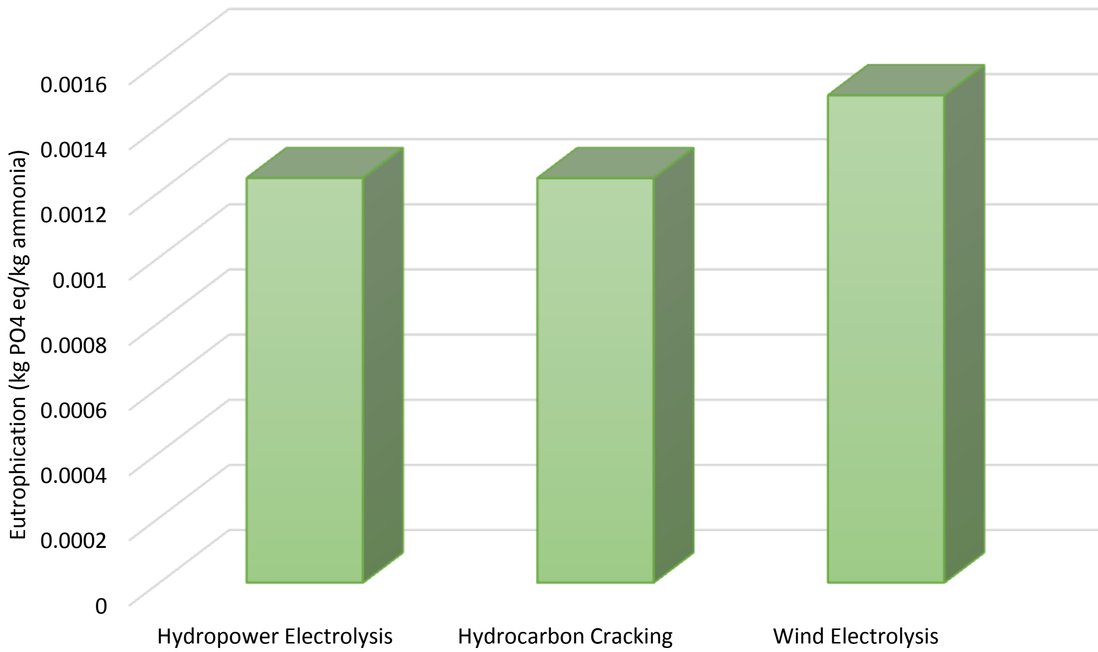

Fig. 8. Eutrophication impact comparison of selected ammonia routes

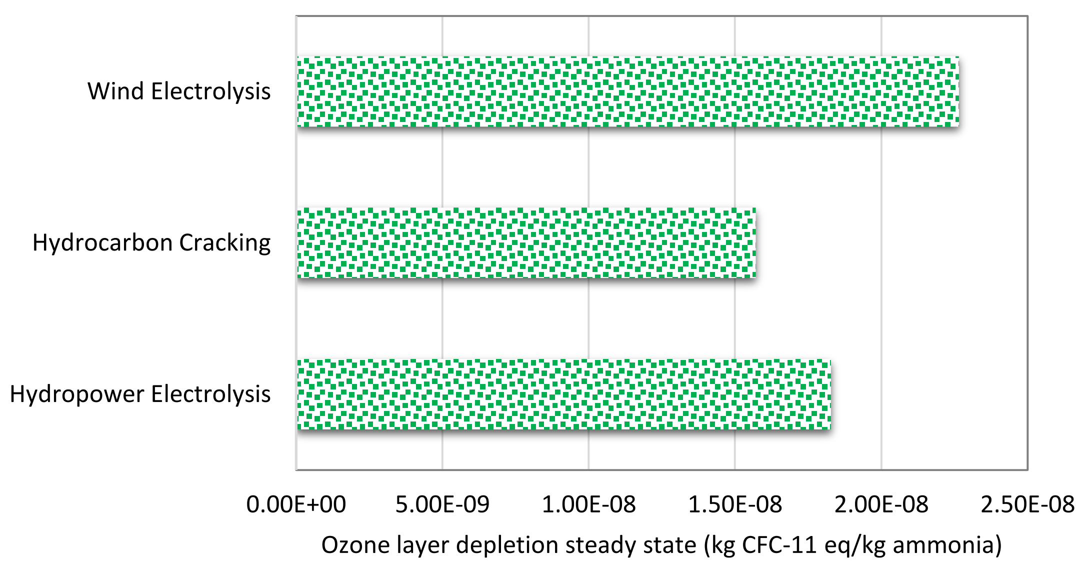

Fig. 9. Ozone layer depletion impact comparison of selected ammonia routes

The production of 1 MJ electricity from residual oil or oil has higher global warming potential than same amount of ammonia production from hydrocarbon cracking method as shown in Fig. 10. This result implies that by replacing ammonia as power generating fuel, total greenhouse gas emissions can be decreased significantly.

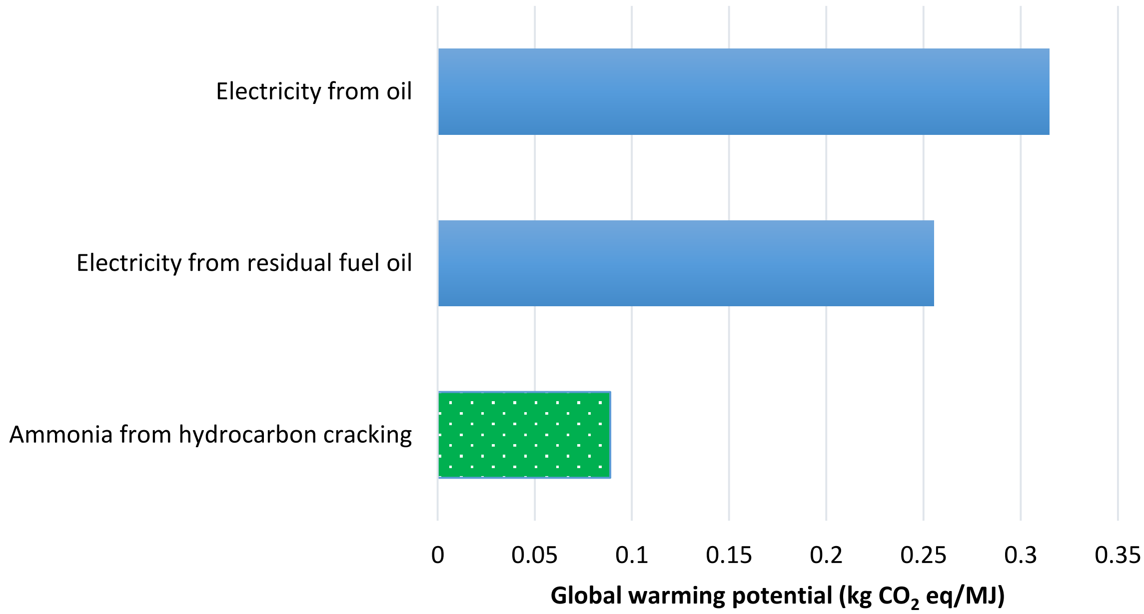

Fig. 10. Comparison of 1 MJ electricity production and ammonia production

Fig. 11 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.

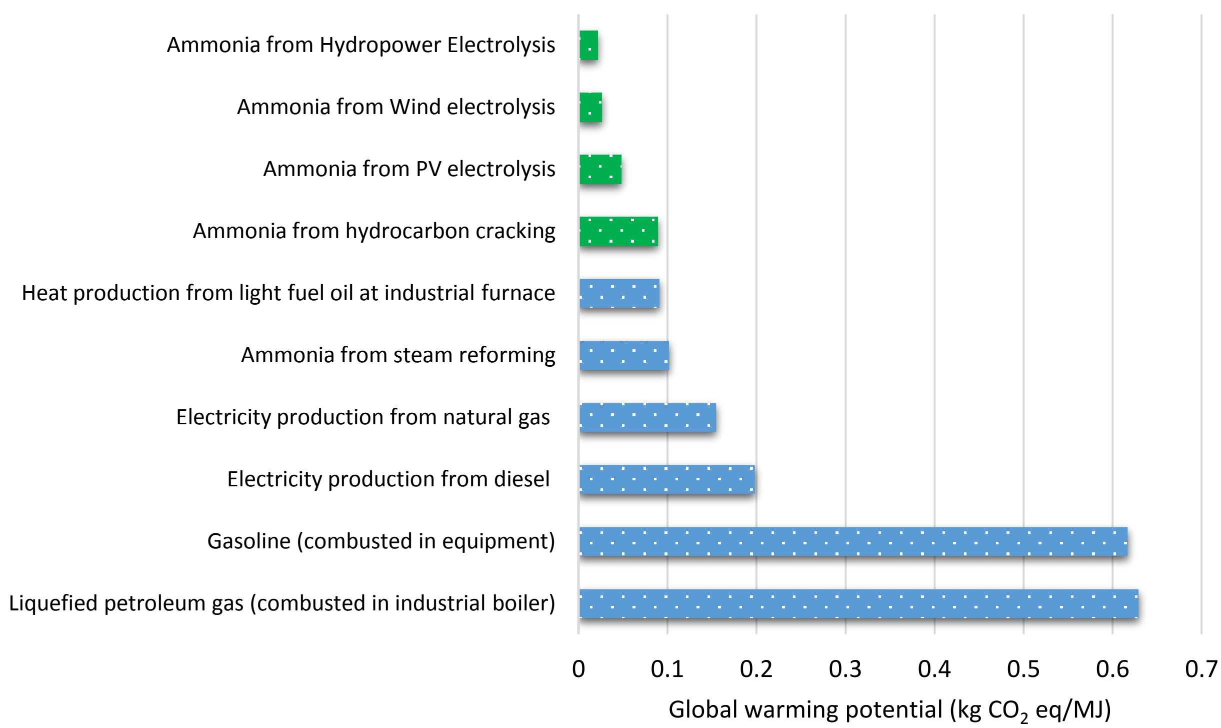

Fig. 11. Comparison of global warming potential of 1 MJ energy production from various resources

2. Closing Remarks

Utilization of hydrocarbons in an environmentally friendly manner becomes more significant day by day. Dissociation of hydrocarbons such as methane and bitumen is a promising option especially for Alberta. Based on the extensive literature review and assessments [10-15], 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.
- 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.
- 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 $/kg.
- The current ammonia retail prices continue to decrease by low natural gas prices. Current retail price is about 550 US$/ton. However, ammonia price is strictly dependent on natural gas price which can be eliminated if oil sand bitumen is utilized.
- Optimized ammonia synthesis using the excess heat in Haber-Bosch ammonia plant for oil sand bitumen extraction which is used for hydrogen production via microwave dissociation process is possible.
- Although hydrocarbon 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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