

and



## Green Ammonia (NH3)

Manufacturing and utlization technologies and research





AIChE Annual Meeting - NH3 Fuel Association Conference: Nov. 1-2, 2017 • Minneapolis, MN.

## C.A.E.C.- Canadian Alternative Energy Corp.

C.A.E.C. was established in 1980 and drove an Ammonia (NH3) fuelled Chev Impala across Canada in late 1981, arriving at a press conference on Parliament Hill in Ottawa called by then Governor General Edward Schreyer on November 5, the same day the deal to repatriate the Constitution a was announced.



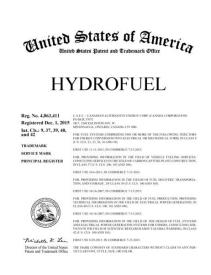
Finance Minister Marc Lalonde driving NH3 car on Parliament Hill, on November 5, 1981

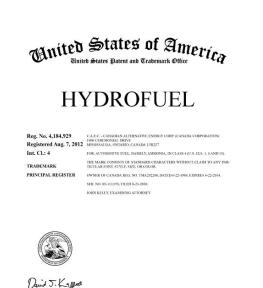


Greg Vezina starting the NH3 car for CBC National News "Back to the Future" news story on November 6, 2006

https://www.youtube.com/watch?v=8vwmzkn0paM

# **C.A.E.C.** is the registered owner of the "Hydrofuel®" Trademarks for six classifications in the US, three in the in EU and one in Canada









#### **Hydrofuel®** Trademark Registrations:

**USA** - (Two marks) under six classifications Reg. #4863411, classes 9, 37, 39, 40, 42 and Reg #4184929, class 4.

**EU** - Reg. #006331854, classes 9, 37, 41.

Canada - Reg. #TMA292288, class 4.



**Hydrofuel**<sup>®</sup> **Inc.** is a leading developer of multi-fuels retrofit conversion systems for engines, generators and vehicles .





Clean Energy Research Laboratory at the University of Ontario Institute of Technology.

Through an option to an exclusive license, Hydrofuel Inc. has been selected as the commercialization partner for the most promising of the University of Ontario Institute of Technology (UOIT)'s ammonia (NH3) and hydrogen technologies, and they have completed several joint research projects.



Developed a new aftermarket multi-fuels conversion system for a 2007 Dodge Ram 3500 Diesel fueled truck and a 2007 Ford Crown gasoline fuelled car to use Ammonia and/or any other liquid fuel.

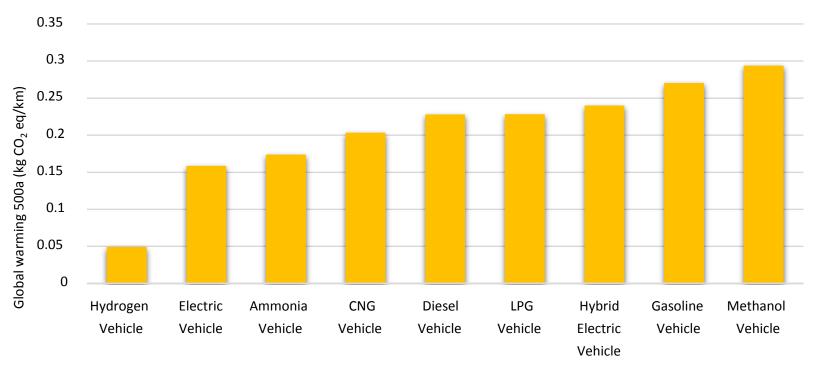






2007 Ford Crown Victoria

UOIT and Hydrofuel's three MITACS research projects, which concluded with the March 2017, 3rd. report, "Comprehensive Evaluation of NH3 Production and Utilization Options for Clean Energy Applications," proves NH3 can be used as a fuel in cars, trucks, buses, locomotives, marine and aircraft applications, and for power storage, generation and combined heating and cooling applications today with lower emissions than all hydrocarbon fuels.



Life cycle comparison of global warming results for various vehicles

Even if ammonia is produced from hydrocarbons, it has similar greenhouse gas emissions with solar energy based route. It is important to emphasize that an ammonia driven passenger vehicle releases less greenhouse gas emissions than compressed natural gas (CNG), liquefied petroleum gas (LPG), diesel, and even hybrid electric vehicles.

CHAPTER 1: QUICK FACTS ABOUT AMMONIA

CHAPTER 2: ELECTROCHEMICAL SYNTHESIS OF AMMONIA

CHAPTER 3: ELECTROCHEMICAL AMMONIA SYNTHESIS FROM PHOTOELECTROCHEMICAL HYDROGEN

CHAPTER 4: FROM HYDROCARBONS TO AMMONIA

CHAPTER 5: AMMONIA IN MARITIME APPLICATIONS

CHAPTER 6: AMMONIA IN AVIATION

CHAPTER 7: AMMONIA IN ROAD TRANSPORTATION

CHAPTER 8: ON-BOARD AMMONIA UTILIZATION

CHAPTER 9: ECONOMIC ANALYSES OF SOLAR ENERGY BASED AMMONIA PRODUCTION

CHAPTER 10: SCALE-UP ANALYSES FOR SOLAR ENERGY BASED AMMONIA PRODUCTION

CHAPTER 11: CONCLUDING REMARKS

#### CHAPTER 1: QUICK FACTS ABOUT AMMONIA - Is ammonia a cost effective fuel?

#### 7. Is ammonia a cost effective fuel?

The illustrative cost comparison of various fueled vehicles is shown in Fig. 2 and 3. 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. 2.

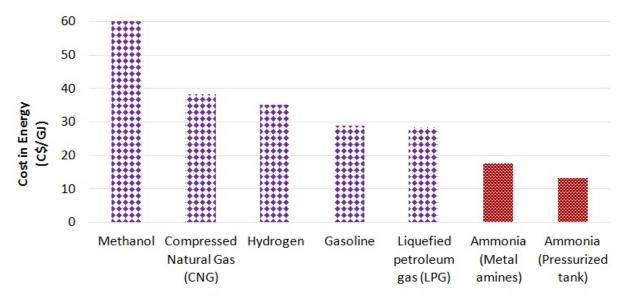


Figure 2 Comparison of various vehicle fuels in terms of energy cost per gigajoule

#### CHAPTER 2: ELECTROCHEMICAL SYNTHESIS OF AMMONIA

#### 4. Concluding Remarks

The electrochemical synthesis of NH3 is a promising alternative to conventional energy intensive NH3 production plants.

Using renewable energy resources to drive the electrochemical NH3 synthesis, the carbon footprint of current NH3 production industry can be lowered significantly.

Electrochemical NH3 synthesis routes offer higher integrability to stand alone and distributed NH3 production which is a carbon free fuel for various sectors.

In this study, NH3 is electrochemically generated at ambient pressure without a necessity of huge compressors using H2 and N2 in a molten hydroxide medium with nano-Fe3O4 catalyst.

The reaction temperature is varied in the range of 200°C to 255°C to investigate the impact of temperature on NH3 production rates.

Having non-corrosive and high surface area nickel mesh electrodes allowed to generate more NH3.

The maximum Faradaic efficiency is calculated as 9.3% with a reaction temperature of 210°C.

The NH3 formation rate is determined to be 6.53×10-10 mol/s cm2 at 2 mA/cm2 current density.

#### CHAPTER 3: ELECTROCHEMICAL AMMONIA SYNTHESIS FROM PHOTOELECTROCHEMICAL HYDROGEN

#### 6. Concluding Remarks

Here, electrochemical synthesis of NH3 is achieved using photoelectrochemical hydrogen. This method appears to be a potential alternative to conventional energy intensive NH3 production plants especially for on-site ammonia production.

The use of renewable energy resources to promote the electrochemical synthesis of NH3, the carbon footprint of the current NH3 production industry can be significantly reduced.

The electrochemical synthesis pathways offer a high potential for NH3 production to separate and distribute a carbon-free fuel for the various sectors. Copper oxide is electrodeposited to have photocathode.

NH3 is electrochemically generated at ambient pressure using photoelectrochemical H2 in a molten hydroxide medium with nano-Fe3O4 catalyst.

The reaction temperature is varied in the range of 180°C to 260°C to investigate the impact of temperature on NH3 production rates.

The maximum coulombic efficiency is calculated as 14.17 % corresponding to NH3 formation rate of  $4.41 \times 10$ -9 mol/s cm2.

It is expected that possible problems in the electrochemical synthesis of NH3 based on liquid electrolytes are further improved by the addition of suitable additives, optimization of the reactor configuration and more resistive materials.

#### CHAPTER 4: FROM HYDROCARBONS TO AMMONIA

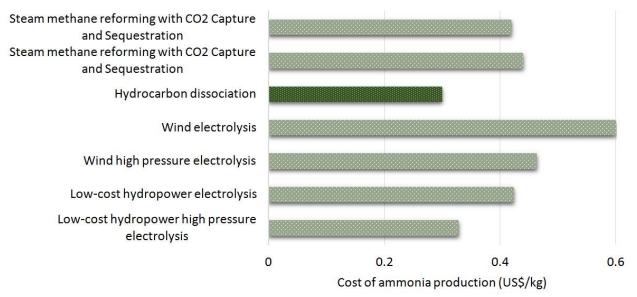


Figure 38 Comparison of cost of production for ammonia using various routes

#### Ammonia was less costly than LNG in 4 Cases studies, Europe, the US, the Middle East and Canada

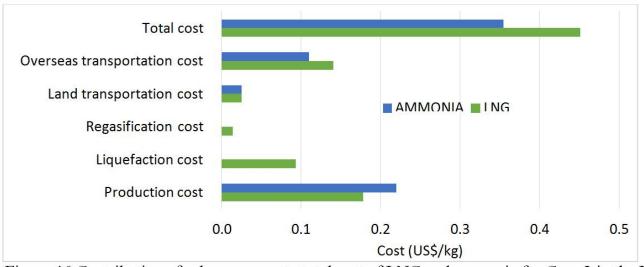


Figure 46 Contribution of sub-processes to total cost of LNG and ammonia for Case 2 in the U.S

#### 4. Oil sand to Ammonia

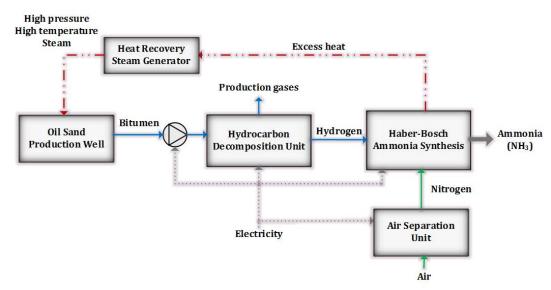


Figure 51 Schematic diagram of oil sand to ammonia plant

#### 5. Concluding Remarks

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 CO2 production.

The microwave energy can be of sufficient power and duration to cause microwave depolymerization of the high molecular weight materials such as bitumen.

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.

#### CHAPTER 5: AMMONIA IN MARITIME APPLICATIONS

Using ammonia as dual fuel in the marine engines can decrease total greenhouse gas emissions up to 34.5% per tonne-kilometer.

For ammonia (hydropower)/heavy fuel oil driven tanker, total GHG emissions are caused by mainly operation of tanker corresponding to about 64% whereas maintenance and operation of port has a share of 31%.

If clean fuels are even partially replaced with current hydrocarbon derived fuels, total GHG emissions in maritime transportation can be lowered significantly.

By development and full utilization of renewable energy based ammonia and hydrogen fuels, GHG emissions during operation of the transoceanic tankers can be even zeroed.

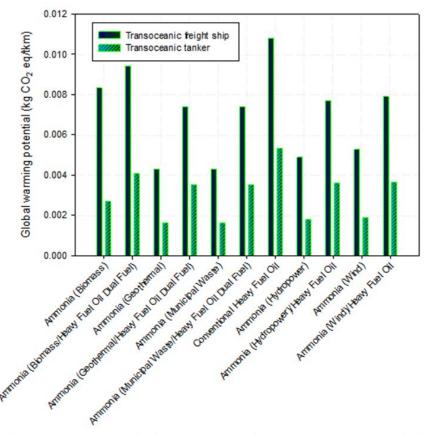


Figure 66 Global warming potential of transoceanic tanker and transoceanic freight ship per tonne kilometer for ammonia and conventional heavy fuel oil

#### CHAPTER 6: AMMONIA IN AVIATION

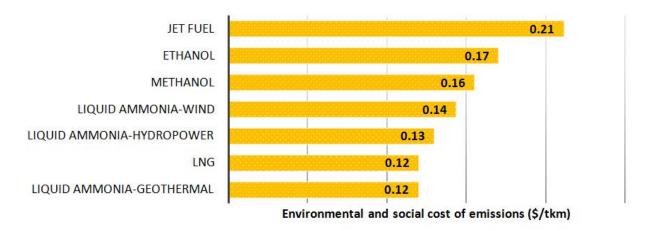


Figure 80 Total environmental and social cost of emissions for various fueled aircrafts from conventional and renewable resources

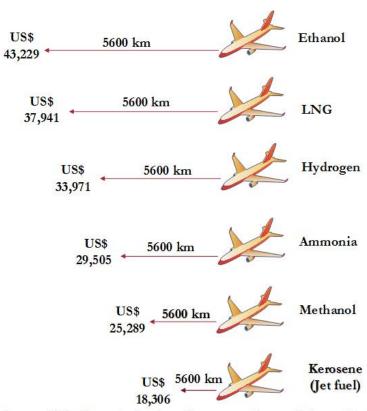


Figure 82 Comparison of fuel costs during the operation of aircrafts for the given range

The performances of the aircrafts in terms of energy and exergy efficiencies in Fig. 83.

In the calculations, two different efficiencies are taken into account namely: production efficiency and combustion efficiency. The production efficiency represent the process from raw material to final product as fuel. The combustion efficiency is the process of utilization in the aircraft.

Here, conventional method (SMR) is taken into account for hydrogen and ammonia rather than renewable based options.

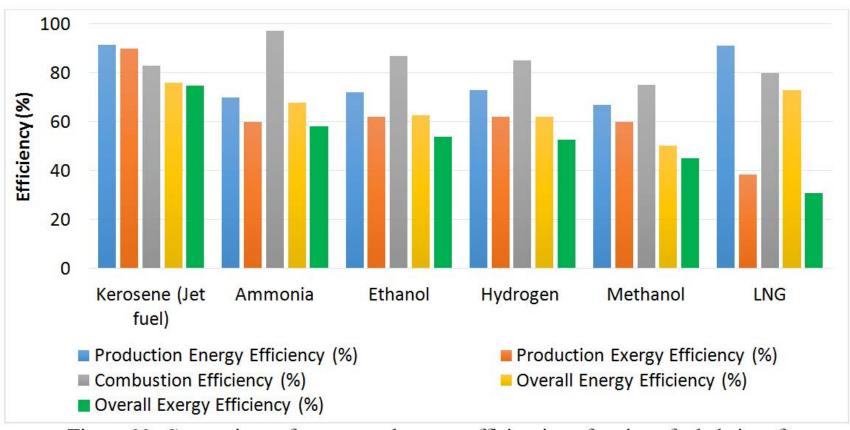


Figure 83 Comparison of energy and exergy efficiencies of various fueled aircrafts

#### CHAPTER 7: AMMONIA IN ROAD TRANSPORTATION

Ammonia can be used for multiple purposes in the vehicle. It is a fuel, refrigerant and reduction agent. The patent developed by UOIT, US8272353 B2 "Apparatus for using ammonia as a sustainable fuel, refrigerant and NOx reduction agent" proposes the utilization of ammonia in these major areas.

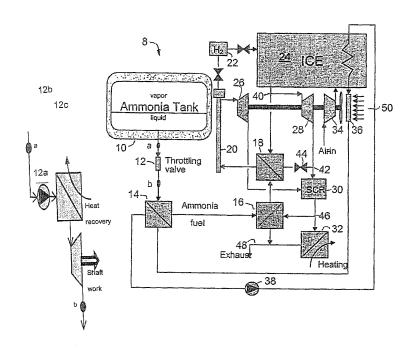
Adaptation of fuel storage tank to store ammonia

A heat exchanger operably connected to the fuel tank

A decomposition and separation unit operably connected to the heat exchangers and having a hydrogen conduit and a nitrogen conduit

The decomposition and separation unit is adapted to separate the heated ammonia into hydrogen and nitrogen and stream them into the hydrogen and nitrogen conduits

An internal combustion engine operably connected to the hydrogen conduit



#### CHAPTER 8: ON-BOARD AMMONIA UTILIZATION

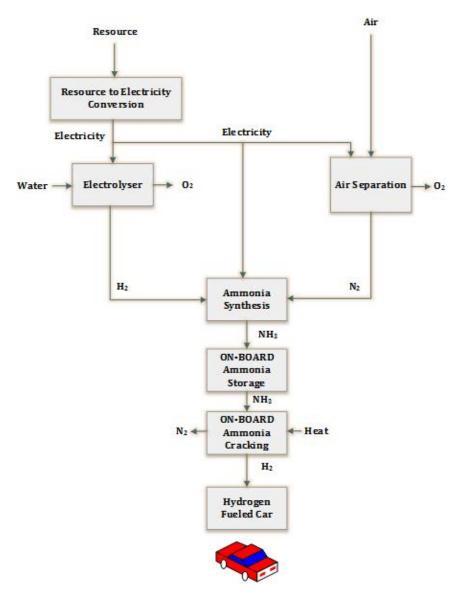


Figure 89 The complete process describing the production, storage and decomposition of ammonia for hydrogen driven vehicle

#### CHAPTER 9: ECONOMIC ANALYSES OF SOLAR ENERGY BASED AMMONIA PRODUCTION

In this section, the exergoeconomic analyses of the experimental systems are performed. The purchased costs of the experimental systems in this study are presented in the following tables. The experimental systems are divided into three main sub-systems;

- Photoelectrochemical hydrogen production reactor
- Electrochemical ammonia production reactor
- Integrated system comprising of solar light concentrator and splitter, PV cell and support mechanism.

The support mechanism used in the integrated system consists of wood and metal parts. The highest cost is for the PEC hydrogen production reactor which corresponds to about 68% of total cost as show in Fig. 102.

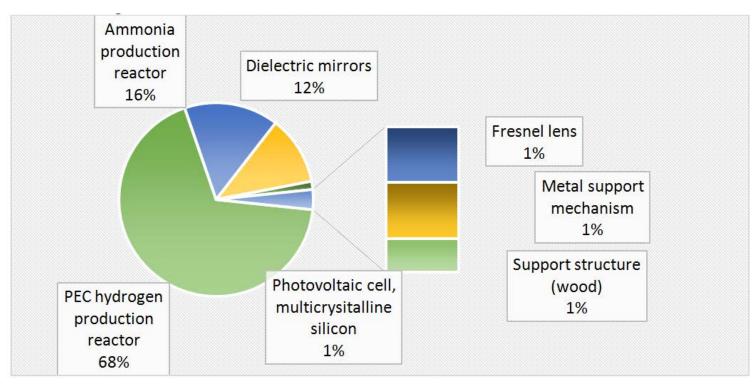


Figure 102 Cost breakdown of the integrated system for hydrogen and ammonia production

#### CHAPTER 10: SCALE-UP ANALYSES FOR SOLAR ENERGY BASED AMMONIA PRODUCTION

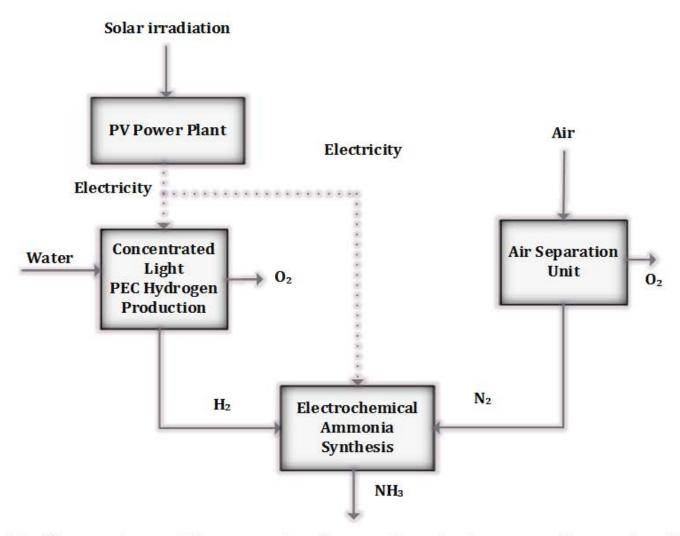


Figure 109 Illustration of large scale electrochemical ammonia production plant

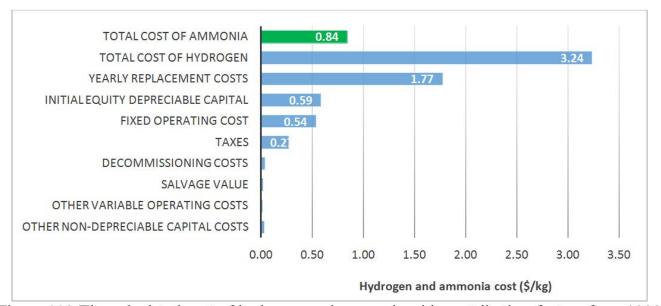


Figure 110 The calculated cost of hydrogen and ammonia with contributing factors for a 1000 kg/day concentrated PEC hydrogen production plant

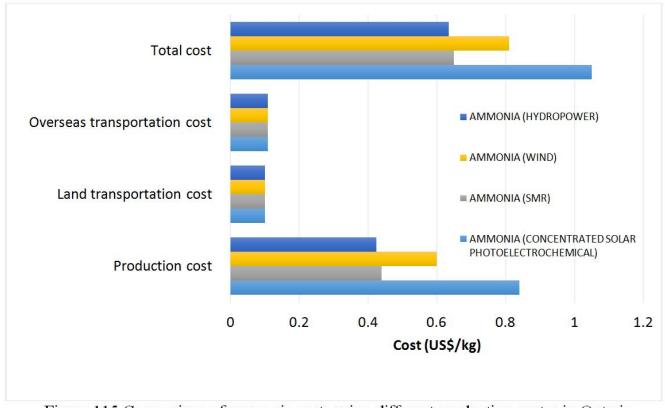


Figure 115 Comparison of ammonia costs using different production routes in Ontario

#### CHAPTER 11: CONCLUDING REMARKS

Renewable ammonia (NH3), which is a carbon-free fuel, refrigerant and working fluid; and storage media of hydrogen, are unique solutions to the world's energy and environmental challenges.

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 significant advantage compared to another type of fuels.

Renewable ammonia and hydrogen can serve almost all economic sectors, ranging from transportation to residential, industrial to commercial, public to utility, and agricultural to chemical.

High-efficiency ammonia/urea plants using natural gas and other hydrocarbon feed stocks can be built beside natural gas power plants and oil sand extraction sites. Utilizing the waste, low-grade heat and excess oxygen results in a significant reduction of costs and emissions.

Dissociation of hydrocarbons such as methane and oil sand bitumen into hydrogen which can be then converted to ammonia is a promising option for oil sand, natural gas and stranded gas reserves.

Ammonia has significant environmental advantages. Even if ammonia is produced from hydrocarbons, it has similar greenhouse gas emissions with a solar energy based route.

An ammonia-driven passenger vehicle emits less greenhouse gas than compressed natural gas (CNG), liquefied petroleum gas (LPG), diesel, gasoline, and even hybrid electric vehicles. They can be utilized for maritime ship engines directly as supplementary fuels or individual fuels.

Ammonia fueled ships yield considerably lower global warming impact during operation. Ammonia as a sustainable and clean fuel in road vehicles yield also the lowest global warming potential after electric and hydrogen vehicles.

# **Hydrofuel Inc.** and **UOIT** will demonstrate the commercial viability of multiple Ammonia Fuel **utilization technologies**

- 1. Aftermarket Conversion Kits for Generators and Engines
- 2. Sell Aftermarket Converted Generators and Engines
- 3. Demonstrate UOIT's Patented high-efficiency Ammonia Heating, Cooling and Power Generating or Vehicle Engine.

Scale-up of technology for NH3 decomposition and separation to generate hydrogen from ammonia for the purposes of installing the system into a generator or vehicle motor engine.

The research project will build on intellectual property which is owned by UOIT: Patent US8272353, CA 2654823 "Methods and Apparatus for Using Ammonia as a Sustainable Fuel, Refrigerant and NOx Reduction".

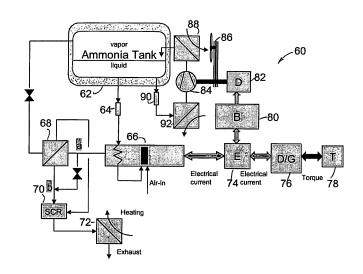
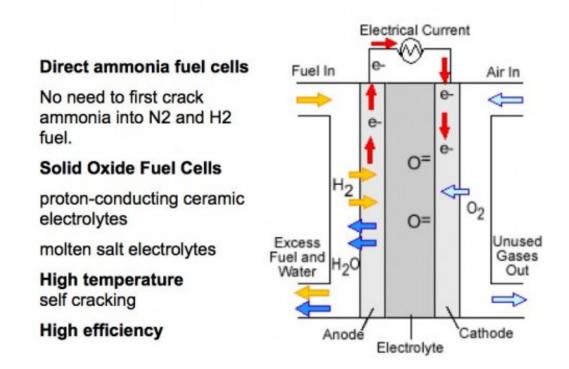


FIG. 5

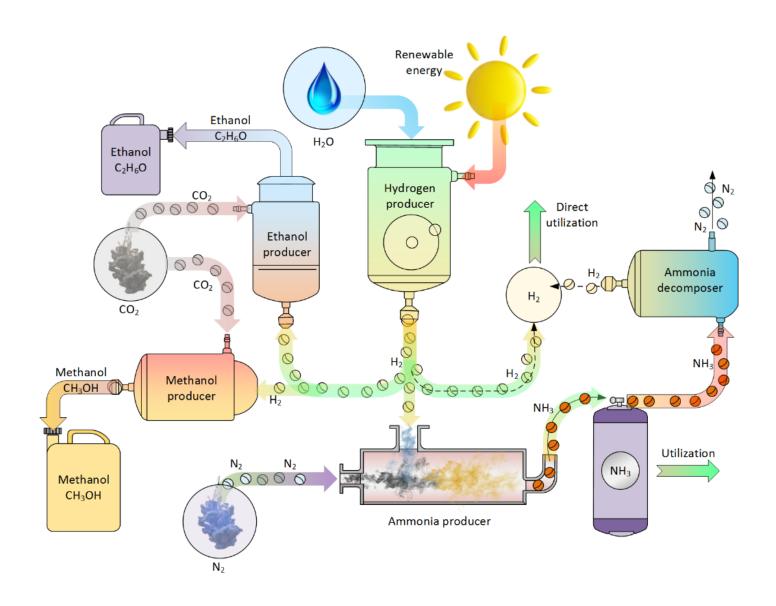
4. Develop prototype direct ammonia fuel cells based on background I.P. of Dr. Dincer's research group at UOIT.



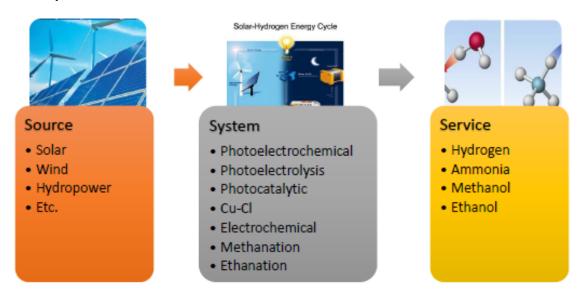
# Commercially demonstrate viability of multiple **UOIT Ammonia production technologies**

Including carbon neutral or negative ammonia made from hydrocarbon and renewable energy sources, and solar NH3

5. Carbon neutral or negative NH3 and methanol/ethanol production from renewable energy including solar



In the process of renewable fuel production, there are many multigeneration opportunities such as heating, cooling and electricity which can easily be integrated to the process in addition to the renewable fuels.



We will also expand our previous work on the manufacture of hydrogen from coal, oil sands, shale, and natural gas below ground to be used to make ammonia above ground on site and leave all the carbon, sulphur and other contaminants and emissions where they are in situ.

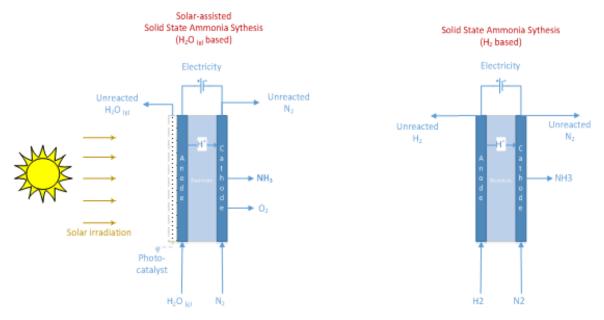
### Ammonia as a solvent for much greener production of oil from tar sands

Solvents to the rescue: how chemistry can save the oilsands industry <a href="http://www.evernote.com/l/ALajwnwQm9ZMFaPWuCUjImv8k\_VISQpnoLY/">http://www.evernote.com/l/ALajwnwQm9ZMFaPWuCUjImv8k\_VISQpnoLY/</a>

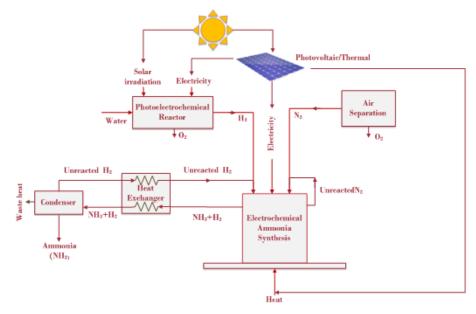
Patent wo2013184506a1 in situ extraction of oilsand with ammonia 2013 alberta oilsands <a href="http://www.evernote.com/l/ALY3Da4HGj9Cqr-ul8Gg3DHDnkczwh1i95M/">http://www.evernote.com/l/ALY3Da4HGj9Cqr-ul8Gg3DHDnkczwh1i95M/</a>

In canada, oil sands companies are teaming up to reduce their environmental impact cosia <a href="http://www.evernote.com/l/ALbFYtZ51ydEXKpPuzVrvW9pDf9MalZJzzM/">http://www.evernote.com/l/ALbFYtZ51ydEXKpPuzVrvW9pDf9MalZJzzM/</a>

# Schematic diagrams of the solid state electrochemical ammonia synthesis method

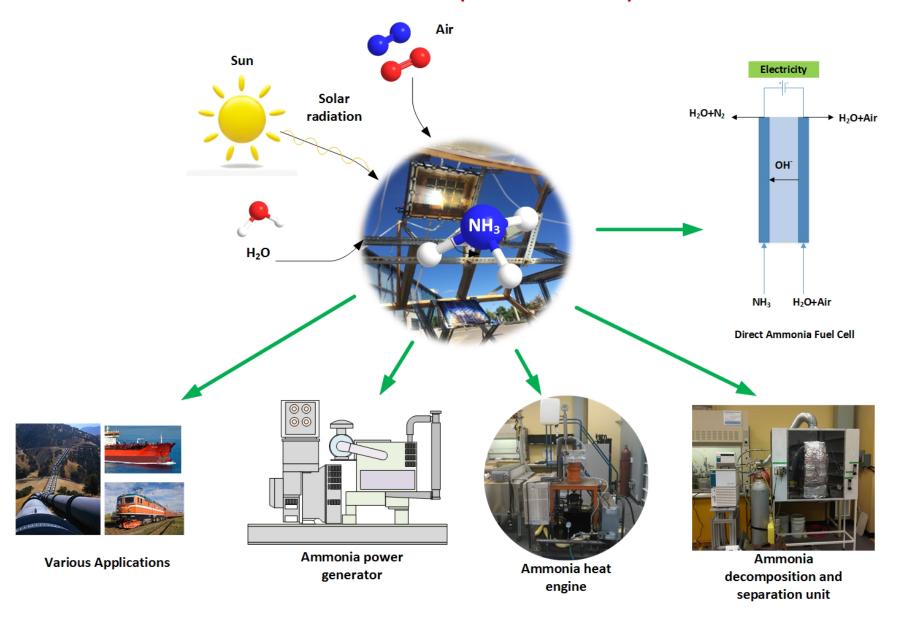


### Schematic diagrams of the green ammonia production



## **UOIT - Hydrofuel "CleAm Tech"© (Clean Ammonia)**

CleAm (Clean Ammonia)





and



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Manufacturing and utlization technologies and research





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