PLASMA ASSISTED HYDROGEN PRODUCTION AND PLASMA CATALYTICAL OXIDATION OF SO2 AND NOX

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1. INTRODUCTION

To solve environmental problems new technologies are in demand. Cold plasma phenomena (e.g. pulsed corona discharges and field electron emissions) can be used to create active species in situ so transport losses can be avoided. The principle is based on emitted high energy electrons. These electrons dissociate molecules and create radicals such as O, OH, N_2 and indirectly HO_2, O_3 and others which again start chemical reactions to oxidize impurities present in gas or water. This makes it possible to convert NO and/or SO_2 into acids and hydrocarbons into CO_2 and H_2O.

The same technology can also be used to develop on-board non-thermal plasma reformers to produce hydrogen-rich gas from hydrocarbons and split water. Plasma boosts partial oxidation reactions. Partial oxidation produces hydrogen-rich gas from hydro-carbon fuels.

Prof. Rusanov from the Kurchatov Institute in Moscow writes on his official website:

"The *large-scale production of cheap hydrogen is one of the basic tasks* of the present-day ecology (and development of hydrogen energy)." …

"Plasmochemical and electrochemical production of hydrogen from water are the basic highly promising and universal processes."

1.1. Excerpt from Jules Verne's book 'The Mysterious Island' (1870)

"... I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable. …

I believe that when the deposits of coal are exhausted we shall heat and warm ourselves with water. *Water will be the coal of the future*."

1.2. Car Engine Builder – Pioneers of Plasma Assisted Technologies

October 2000:

PSA Peugeot Citroen and Delphi signed development agreement to apply non-thermal plasma exhaust aftertreatment to future Peugeot Citroen vehicles. Delphi reported that its plasma-assisted catalyst system, in steady-state testing of a diesel vehicle, has demonstrated greater than 65% reduction of NOx emissions without additional hydrocarbons to the exhaust stream, greater than 85% with additional hydrocarbons, as well as a "significant reduction in particulates".

October 1997 – May 2004:

DaimlerChrysler and partners were funded by the German Federal Ministry for Education and Research (BMBF) for project "Laserdiagnostic and Plasmatechnological Foundations to Reduce Emission and Fuel Consumption of Diesel Combustion Motors". There are several other German companies and universities involved.

1.3. New Trends in Aerospace Business Towards Plasma Technologies

June 1999 – November 2002:

EADS Research Center Ottobrunn and partners were funded by BMBF for project "Exploration of New Homogeneous Atmospheric Plasmas and Selected Applications".

March 2004:

To meet future environmental quality goals, Rolls-Royce Deutschland published that in the time horizont to the year 2020 one major technology task would be the *development of plasma catalytical oxidation of SO2 and NOx* [1].

And in the time horizont after 2020 the technology task is the *development of zero emission vehicles based on fuel cell generators* for speculative rotating electrostatic (plasma) wave "propellers" having no moving parts [1].

2. PLASMA ASSISTED HYDROGEN PRODUCTION

2.1. Biological Hydrogen Production

2.1.1. Cold Hydrogen Production by Blue Algae

The idea of biophotolysis of water is based on the integrated metabolism between vegetative cells and heterocysts in blue algae, where hydrogen is required for nitrogen fixation. The blue alga *Nostoc muscorum* splits water. The process is driven by the energy of light. FIG 1 shows the blue algae and the schematics for the process.

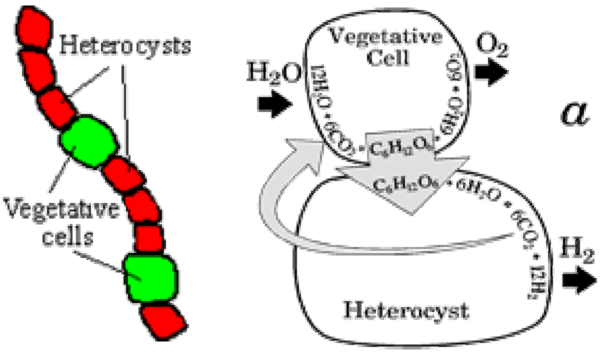

FIG 1. Blue alga *Nostoc muscorum* and biophotolysis.

2.1.2. Hydrogen Production by Artificial Bacterial Algal Symbiosis

Since 1987, Rechenberg works on the artificial bacterial algal symbiosis using purple bacteria and green algae. Process is driven by light energy [13], [14].

Purple bacteria carry out a biological HABER-BOSCH process which is a catalytical ammonia-synthesis:

(1) $N2 + 3 H2 \rightarrow 2 NH3$.

But if nitrogen is not available, purple bacteria produce only hydrogen. The vegetative cell of *Nostoc* corresponds with the flask containing green algae. Here the hydrogen of the water will be built in Carbohydrates (algae excretes). The carbohydrates are transported through a special membrane into the heterocyst, which corresponds with the flask containing purple bacteria. Here the carbohydrates are broken into CO2 and H2 by means of nitrogenase.

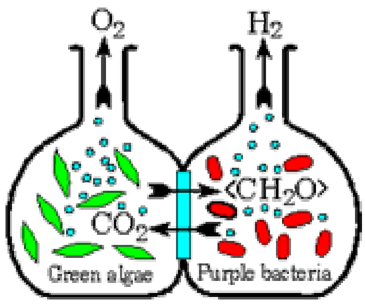

FIG 2. Artificial bacterial algal symbiosis.

2.2. Technological Hydrogen Production

It is the thought of bionics to use artificial systems in place of the evolved originals in nature. For a future biophotolysis of the water hydrogen could be binded to a carbohydrate-analogue in a first stage. The hydrogen-complex, unable to re-react with oxygen, then moves to a second stage, where the hydrogen will be released. The blank carrier molecule moves back to the first stage, where it is reloaded with hydrogen. — But a solution à la bionics is not in sight [13]. The major problem is the large-scale production. In this context plasma chemistry could help.

2.2.1. Plasma-Assisted Hydrogen Production from Hydrocarbons

What are the tricks to produce enough hydrogen on board a car or an airplane to keep fuel cells generating electricity and moving the engines ?

First Step:

Development of on-board *non-thermal plasma reformers* to produce hydrogen-rich gas from hydrocarbons, also for regeneration of NOx.

Breakthroughs by leading scientists in this new research field from MIT (USA) [2], Kurchatov Institute (Russia) [3] and Ruhr-University Bochum (Germany) [4].

Power	50-500 W.
Voltage	500-20000 V
Current	15-120 mA
Flow rates H_2	30-50 liters/min
Height	20 cm
Volume	2 liters

TAB 1. Parameters of low current plasma fuel converter.

The required electrical energy input to the plasma fuel converter is on the order of 2% of the heating value of the fuel. Typical reforming efficiency in partial oxidation mode of operation was around 70% (ratio of heating value of the H2 rich gas to heating value of the fuel). FIG 2 shows a schematics of the MIT Plasma Reformer.

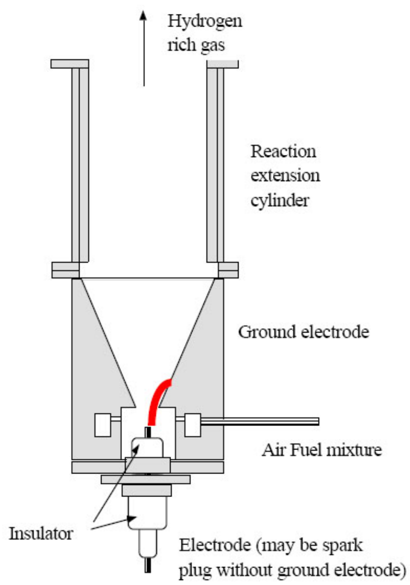

FIG 3. MIT Plasma Reformer [2].

Plasma reformers:

Plasma boosts partial oxidation reactions. Partial oxidation produces hydrogen-rich gas from hydro-carbon fuels.

The stoichiometric partial oxidation is described by

(2) $CmHn + m/2\ (O2 + 3.8\ N2) \rightarrow mCO + n/2\ H2 + 1.9\ N2$.

For iso-octane (representative of gasoline) the equation is

(3) $C8H18 + 4\ (O2 + 3.8\ N2) \rightarrow 8\ CO + 9\ H2 + 15.2\ N2$.

15% of energy is released in partial oxidation of gasoline.

Here are some parameters for Diesel applications:

Plasmatron electrical power:	220 W
Diesel Flowrate:	0.31 g/s
Hydrogen flow rate:	26 liter/min
Energy Consumption	6.2 MJ/kg H2

Product Gas Composition, Vol.%

H2 18.2	N2 58	
CO 19.8	CO2 3.8	CH4 0.3 .

3. PLASMA CATALYTICAL OXIDATION OF NOX

Cold plasma technologies can also be used to oxidize NOX and SO2 (*plasma exhaust aftertreatment*).

3.1. Theory for Plasma Catalysis

The principle is based on high energy electrons. These electrons dissociate molecules and create radicals such as O, OH, N2 and indirectly HO2, O3 and others which again start chemical reactions to oxidize and convert NOX and/or SO2.

3.1.1. Non-Thermal Plasma Treatment of NOx in Engine Exhausts

A plasma reactor using pulsed corona discharges produce a plasma with an average electron kinetic energy of around 3 – 6 eV.

Kinetic energy of the electrons is deposited primarily into the major gas components, N2 and O2.

Most useful deposition of energy associated with the production of N and O radicals through electron-impact dissociation are

(2) $e + N2 \rightarrow e + N(4S) + N(4S, 2D)$,

(3) $e + O2 \rightarrow e + O(3P) + O(3P, 1D)$,

where N(4S), O(3P) and N(2D), O(1D) are ground-state and metastable excited-state nitrogen and oxygen atoms, respectively. O(3P) is simply referred to O.

N (4S) is the only plasma-produced species that could lead to chemical reactions of NO:

(3) $N(4S) + NO \rightarrow N2 + O$,

But the N(2D) species reacts with O2 to counterbalance NO reduction again:

(4) $N(2D) + O2 \rightarrow NO + O$.

Dissociation energy of O2 is smaller than that of N2. So oxidation is only pathway for NO conversion.

Under this condition the rate for electron-impact dissociation of O2 is much higher compared to the dissociation of N2. The dissociation of O2 will produce only oxidative radicals. So the ground-state oxygen atom, O(3P), will convert NO to NO2 via

(5) $O(3P) + NO \rightarrow NO2$

(6) $O(3P) + O2 \rightarrow O3$

(7) $O3 + NO \rightarrow NO2 + O2$

The metastable oxygen atom O(1D) will react with H20 to produce OH radicals

(8) $O(1D) + H20 \rightarrow 2\ OH$.

The OH radicals will convert NO to NO2 to nitrous and nitric acid (HONO2). Furthermore oxidation can happen by hydrocarbon radicals:

(9) $NO + R02 \rightarrow NO2 + RO$.

3.2. Jet Propulsion Applications

There are few reports about tests in jet engine and missile test cells discussing the feasibility at flow rates of jet engines [5]-[8], [11]. It was shown that pulse-corona-induced plasma technologies could remove up to 90% of NOx from combustion exhaust under (small scale) laboratory conditions equivalent to the JETC environment. The conclusion was that cold-plasma-discharge technology is completely practical at much larger scales than are currently being investigated [11]. The same report gives also recommendations to further develop this technology as an emission control for applications to decontamination of combustion exhaust streams [11]. “As the trading value of emission credits continues to increase, it is reasonable to expect that both military installations and aircraft-related industries will encounter circumstances in which applying a control to an engine testing facility crosses the economic threshold of practicality.” [11]

4. CONCLUSION

Car engine builders are currently pioneering plasma assisted combustion and exhaust aftertreatment technologies. Breakthroughs for Diesel car engines: on-board plasma assisted hydrogen production from hydrocarbons is feasible. Breakthroughs in on-board plasma-assisted hydrogen production from water is soon expected.

Plasma catalytical oxidation of NOx is feasible at least in car engines.

Indications from unclassified military research reports that plasma catalysis also works in jet engines with high flow rates. There is need for breakthrough in material sciences (development of efficient carbon nanotube and diamond-like-carbon field electron emitters at low voltage).

Aerospace companies show increasing interest in plasma assisted combustion and flow control technologies.

5. OUTLOOK

The current focus at the Institute of Bionics and Evolution-technique is on electrostatic (plasma) wave propulsion and flow control [15], [16] but the same generators can also be used to develop non-thermal plasma reformers to produce hydrogen-rich gas from hydrocarbons and hydrogen from water. This will be studied in future project using the high voltage power supply shown in FIG 4.

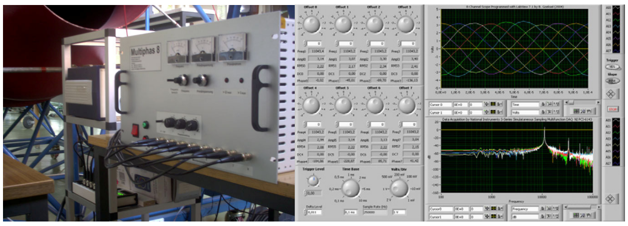

FIG 4. Polyphase high voltage power supply.

Characteristics of the Polyphase High Voltage Power Supply shown in FIG 4:

- Maximum average power (for 8 outputs): 300 Watt

- Maximum output voltage: 3-6 kV

- Pulse frequency range: 5-50 kHz

- fast current monitoring: maximum current 25 mA

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