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# Non – equilibrium plasma assisted hydrogen production: State-of-the-art

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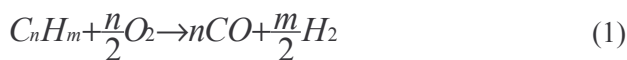
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On-board hydrogen production by means of hydrocarbon reforming systems could lead to interesting alternative for the development of fuel cells in vehicles. In order to meet supply requirements for those vehicles, non equilibrium plasma based technologies have been implemented over the two last decades; using various plasma types such as plasmatron [1], gliding arc [2]-[8], dielectric barrier discharge (DBD) [9][10], corona [12], microwave [13][15] or pulsed discharge [16]. This state of the art aims to provide an overview of the setting up, feasibility and efficiency of the existing test bench, and so highlight key characteristics of plasma reforming. Performances have been calculated and compared against each other [17].

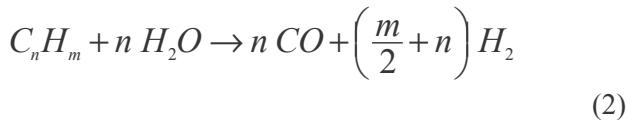
## 1. Introduction

Recent years have seen a real enthusiasm for fuel cell development as a good alternative to fuel (diesel, gasoline) based combustion engines in terms of efficiency and environmental impact. The technology based on hydrogen however has significant drawbacks due to its storage properties: hydrogen is characterized by a very low volumetric heating value as a result of its low density (2.016 g/mol) : 11 kJ/l at atmospheric pressure against 16000 kJ/l for methanol. In response to the storage problematics, one possible way to ensure the feed in of hydrogen on the vehicle would be to store it as liquid fuels (methanol, gasoline...) and then to produce hydrogen out of these fuels: this chemical transformation is called reforming; and is an oxidation reaction in which oxygen, water or carbon dioxide play the role of the oxidant. Thus, three main reforming reactions are possible:

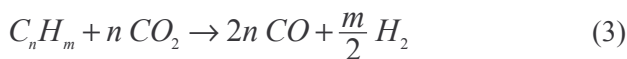
- Partial Oxidation (POx)



- Steam Reforming



- Dry CO<sub>2</sub> Reforming



The partial oxidation is strongly exothermic whereas the steam reforming and the dry CO<sub>2</sub> reforming are endothermic. Non equilibrium plasmas have been applied for flue gas treatment and have been considered very promising for organic synthesis because of their non-equilibrium properties, low power requirement and their capacity

to induce physical and chemical reactions within gases at relatively low temperatures.

## 2. Presentation of the technologies employed

In this section are presented the major works in the field of non-equilibrium plasma assisted reforming.

The Plasma Science and Fusion Center (MIT, USA) is one of the most advanced in plasma assisted reforming. Bromberg and co-workers have developed two plasmatrons called GEN2 and GEN3, work at constant current [1] (GEN2: 15-120 mA, corresponding to power in the order 50-300 W).

Fridman *et al.* (DPI, USA) have studied [2], [3], [12] the use of corona discharges ( power of the plasma source varying from 1 to 20 W) and gliding arc. Second reactors aimed higher power, especially the gliding arc in tornado reactor, originally based on reverse vortex flow (high voltage DC power supply delivering power around 200W).

The Groupe de Recherches sur l'Energétique des Milieux Ionisés (France) has been working on different kinds of reactor [5], [6]: three-discharge glidarc (RotArc), magnetic blow out glidarc reactor, electrical discharge, sliding discharge .

Czernichowski (ECP, France) is considered to be the inventor of the gliding arc principle [4], [19]. He worked on various fuel reforming on a reactor called Glidarc I. Power supplied varied from 0.6 to 1.1 kW.

Hammer *et al.* (Siemens AG, Germany) have successively developed three reactors [9], [21]: DBD, low energy electron beams and then later arc discharge. This evolution aimed higher hydrogen yields and energetic density.

The Center for Energy and Processes (EMP, France) has been studying plasma applications to hydrocarbons conversion through two successive reactors based on gliding arc technology [7], [8], [22]. Second one was supplied with a current source

and based on a resonant converter technology (maximum values: 15 kV, 660 mA.).

The Department of Applied Chemistry (Waseda University, Japan) has developed a non-equilibrium pulsed discharge reactor and a diaphragm reactor [16], [23], [24]. Electrical power is typically under 100 W. Attention was focused on the generation of the discharge in the liquid phase.

Two departments of the Tokyo Institute of Technology (Japan) have been studying plasma assisted reforming [10], [13]; first one thanks to a micro scale non-equilibrium reactor and then a DBD reactor coupled to a catalyst; while the second department used a microwave discharge.

At Kurchatov Institute Russian Research Center (Russia) [14], [15], [26] have been investigated partial oxidation with two types of microwave discharge: a pulsed periodic regime (streamer pseudo corona discharge, pulse power up to 3 kW, and a continuous regime (coaxial torch discharge, 2.45 GHz frequency and power in the range 1-5kW).

A DBD reactor [11] has been developed at Laboratoire de Physique des Gaz et des Plasmas (France), delivering voltages in the range and up to 40 kV and function either pulsed or in alternative currents (up to 120 Hz).

### 3. Comparison of non-equilibrium plasma assisted reformer performances

#### 3.1. Definitions of the terms employed

In order to make comparisons on the same basis, efficiencies and conversion rates have been calculated as defined below :

##### a. energetic efficiency

Fuel reacts with oxygen or water to produce hydrogen, whose heating value is higher than any other hydrocarbon. Therefore, the efficiency of a reforming system is the Lower Heating Value (LHV) of hydrogen produced divided by the input energy, that is the summation of the electrical energy of the plasma and the Lower Heating Value of the hydrocarbon injected.

$$\eta = \frac{(H_2 + CO)_{produced} \times LHV(H_2)}{PlasmaEnergy + LHV(fuel)} \quad (4)$$

We consider that the entire CO produced is then converted into H<sub>2</sub> by Water Gas Shift reaction. Therefore, we take into account the CO produced.

##### b. conversion Rate

In order to produce hydrogen, hydrocarbon molecules have to be "cracked", to break the C-C and C-H links. The performance of this operation is evaluated by using the conversion rate which the

ratio of atomic carbon contained in reforming products to the atomic carbon contained in the injected hydrocarbon:

$$\chi = \frac{[CO + CO_2 + CH_4 + \dots]_{produced}}{n \times [C_n H_m]_{injected}} \quad (5)$$

The efficiency and the conversion rate as defined in equations (4) and (5) appear to be good indicators for quantifying reforming systems performances. Both parameters have been calculated for non-equilibrium plasma processes data found in the literature (see section 2), when available. As a result, some values reported here could be different from those claimed by the authors in their articles or proceedings.

Figure 1 and 2 illustrate the efficiency and the conversion rate. The figures contain information on the hydrocarbon feedstock, the non-thermal plasma device as well as the institution involved in the development of the plasma technology. Notice that most of the results published concern arc discharge based technologies.

#### 3.2. Comparison of energetic efficiency

Figure 1 includes 121 entries collected from literature. Efficiency distribution is widely spread from 0.49% to 79%. The highest values correspond mainly to arc discharge. The GAT reactor achieves the top value with 79%.

#### 3.3. Comparison of conversion rates

Figure 2 contains 113 conversion rate entries, which have been worked out from data found in publications. Notice that some results are greater than 100%, which might be due to some approximations done for the gas analysis.

Conversion rate reports to how much hydrocarbons has gone through the plasma region, how much C-H links have been "broken". Therefore, the homogeneous nature of the plasma zone can be evaluated. The gliding arc has been first developed for an arc igniting and increasing in the plane of two electrodes. This two dimensional set up leads to weak conversion rate because a small part of the gas mixture would go through the arc. As a consequence, further improvements concerned three dimensional construction (plasmatron GEN 2 and 3, GAT, Glidarc I, plasma torch) and showed then good conversion capabilities. This has to be taken into consideration together with the fact that arc discharge is a high energetic density mean. At last, in arc discharge system can appear a flame phenomenon that is also involved in the conversion process.

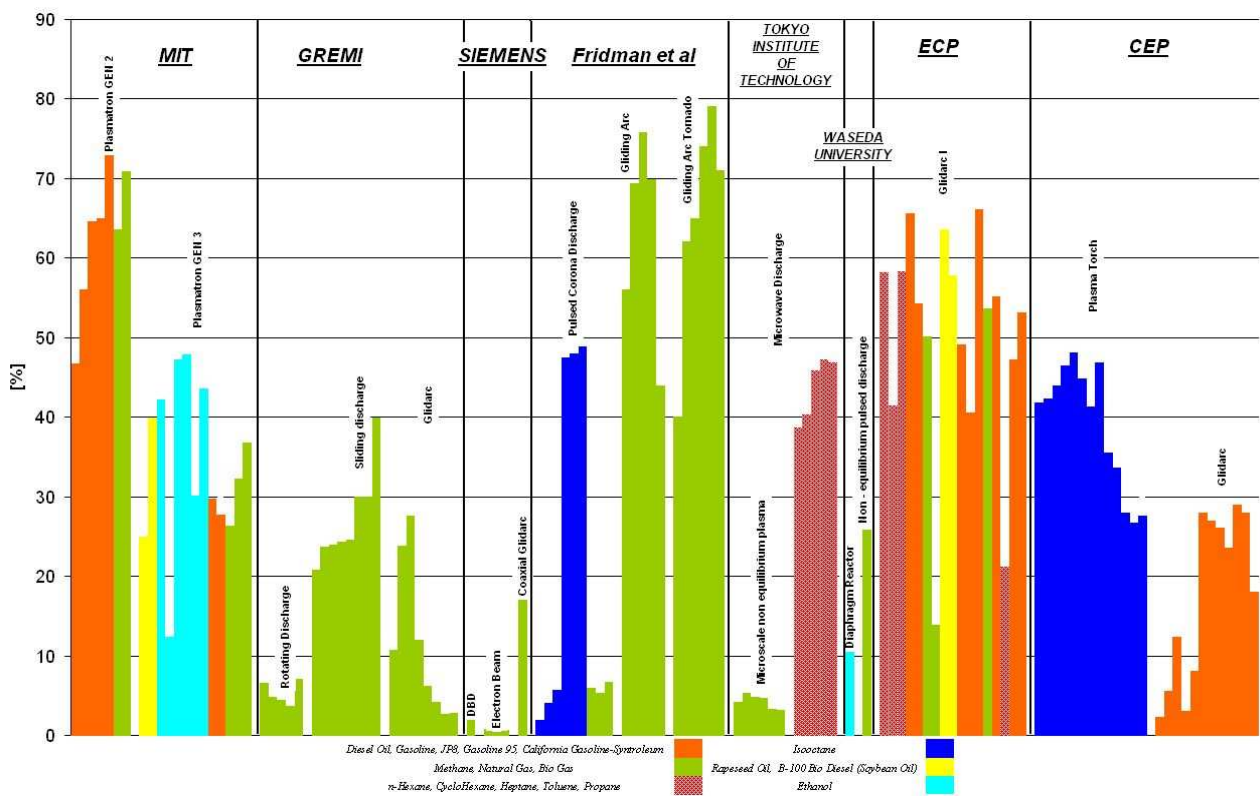


Figure 1. Energetic efficiencies of different non-equilibrium plasma assisted technologies

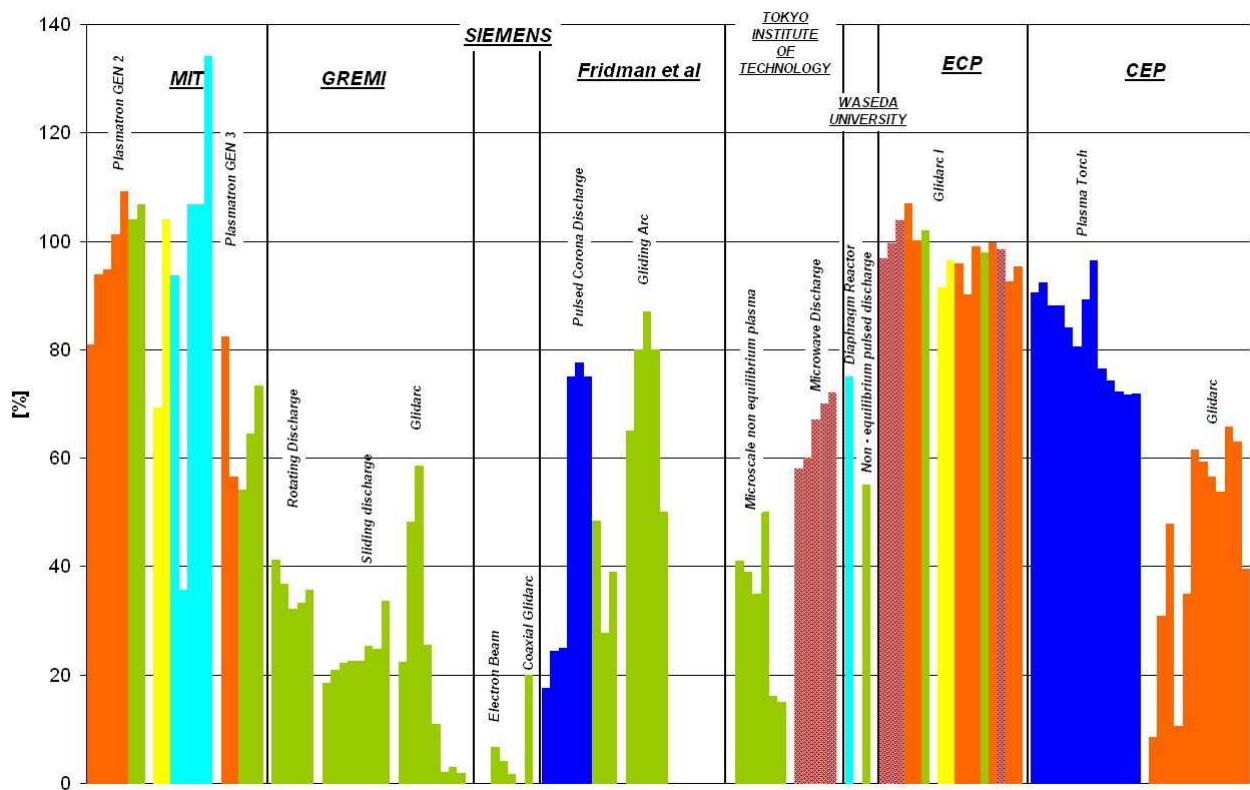


Figure 2. Conversion rates of different non-equilibrium plasma assisted technologies



#### 4. Conclusion

In the field of assisted production of hydrogen, non-thermal plasma reforming exhibits interesting results in terms of efficiency, conversion rate and H<sub>2</sub> yields.

Non-equilibrium plasma reforming reactors are still being developed and further advanced in research laboratories. Most of the studies performed have concerned the development of the non-thermal plasma assisted reforming, through the investigation of various fuels and plasma types. The review of their set up gives characteristic keys such as technology and operating conditions. In addition, comparisons of their outputs (efficiency, conversion rate...) show that arc discharge based technologies meet the best performances because of their relative simplicity of set up, their high energetic densities and their ability to create a large reactive volume.

Non-thermal reforming for onboard applications is relevant: good H<sub>2</sub> yields, compactness, reactive system, non-deactivation because of coke deposition, sulfur presence or high temperature. However, the technology is not mature yet and more works have to be made in order to compare it with existing onboard catalytic systems. The lack of information concerning mainly performances during transient regimes (cold start-up, acceleration, shutdown...) and NO<sub>x</sub> production (when air is used – ATR or Pox) makes the evaluation of the technology for onboard applications difficult.

#### Acknowledgements

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