



Renewable Hydrogen

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The Need of Hydrogen as One of the Future Energy Carriers

The world energy generation based on fossil fuels burning is having a serious impact on the world ecology and economy. In contrast, hydrogen is an energy carrier, with better social, economic, and environmental benefits to its credit than fossil fuels. Fundamentally: less emissions, more accessible sources, renewable sources, control of the sources and more efficient conversion devices

What is Needed to Implement the Use of Hydrogen as an Energy Carrier?

The fundamental components, necessary to put in place, for the introduction of hydrogen as an energy carrier, are analogous to those in today's energy systems, that is:

- production
 - purification
 - delivery
 - storage
 - conversion
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Hydrogen in Transportation and Stationary Applications

One of the major applications of hydrogen will be to feed a fuel cell in order to produce electricity to power electric motors in order to move cars and trucks. Other use is for feeding efficient converting stationary devices, such as, fuel cells to produce electricity

Why Fuel Cells?

In the case of transportation issues fuel cells have three times the efficiency of internal combustion engines. On the other hand for stationary applications fuel cells have twice the efficiency of turbines

Current Hydrogen Production

The present hydrogen production totalizes: 4.5×10^{10} kg/year; this amount, if used to generate energy, will satisfy, only, 2% of the energy demand; but, it is not intended for energetic purposes, it is rather used in the production of: methanol, ammonia and also in oil refining processes [1,2]

Current Hydrogen Sources

About 96% of the present hydrogen production is obtained from fossil fuels, specifically: natural gas steam reforming (48%), naphtha reforming (30%) and coal gasification (18%); that is, nonrenewable sources which give rise to nonrenewable hydrogen which generates greenhouse gas emissions [1]. The other 4% are obtained by electrolysis [2]

How Far is Hydrogen, as a Widespread Energy Carrier

The complete technology to begin the switch from a petroleum-based economy to an economy where hydrogen is one of the energy carriers will become accessible in about ten to twenty years. But, for this to take place, it is needed to develop, on the one hand, the related Hydrogen Science and Technology and on the other hand a huge investment program in order to get the necessary amounts of hydrogen to produce energy

Renewable Hydrogen

Currently exist the capacity to produce hydrogen from different sources, for example: methane, propane, gasoline, light diesel, biodiesel, methanol and ethanol, between others substances. The problem is how to obtain these resources from renewable supplies that will prove to be efficient

Why Renewable Hydrogen?

If the production of hydrogen is carried out from fossil fuels, we are not taking advantage of three of the major benefits of hydrogen, that is: less emissions, control of the sources and accessibility of the sources

Ways to Produce Renewable Hydrogen

Currently, in very general terms, is possible to identify three fundamental forms to produce, non biological, renewable hydrogen:

- water splitting
 - thermal treatment of biomass: pyrolysis and gasification
 - steam reforming of organic compounds obtained from biomass
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Water Splitting

With the help of:

- **thermal cycles: powered with nuclear or solar energy**
 - **electrolysis: producing the electricity, with: wind, geo-thermally, nuclear or solar energy or with a hydroelectric plant**
 - **photolysis by photo-catalysis, energized with solar energy**
 - **combination of thermal and photolytic processes**
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Biomass

Some biomass sources are [3]:

- municipal solid waste
 - sewage sludge
 - industrial waste
 - agricultural waste
 - sugar cane
 - herbaceous crops
 - wood industry residues
 - forest resources
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US Agricultural and Forest Biomass Production

The Department of Agriculture of the US (USDA) and Oak Ridge National Laboratory calculated that the U.S. can produce 1.3×10^{12} kg of dry biomass/ year with the help of its agricultural (72% of total) and forest (28% of total) resources; where this amount of biomass has the energy content of 3.8×10^9 boe (barrels of oil energy equivalent) and the U.S. consumes 7×10^9 bbl (barrels of oil)/year [4]

Pyrolysis

Pyrolysis consists in the thermal treatment of biomass at a temperature from 400 to 500 C and a pressure from one to five atmosphere in the absence of air to get: H_2 , CH_4 , CO , CO_2 and other gases depending on the biomass; and also, liquid products, as tar and oils, and solid products as, char, carbon and other inert solids [3,4]

Gasification

Gasification is a thermal treatment of biomass at temperatures higher than 800 C in the presence of oxygen and/or water [3]. During this procedure are generated gases (CO, H₂, CO₂, CH₄, and N₂) which can be steam reformed to produce hydrogen [4]. Additionally, the production of hydrogen can be increased with the help of the water–gas shift reaction [5]

Reactions Taking Place During Gasification

- **partial oxidation:** is a reaction which use less than the stoichiometric quantity of oxygen needed for total combustion
- **steam reforming:** is a the reaction between water vapor and the biomass-derived feedstock (methane for example) to produce CO, CO₂, and H₂.
- **the water-gas shift:** is a reaction where water vapor and CO react to generate H₂ and CO₂
- **methanation:** is a chemical process where CO and H₂ react to form CH₄ and H₂O

Steam Reforming

Some products, obtained from biomass, which can be steamed to produce hydrogen are:

- ethanol
 - methane
 - biodiesel
 - glycerol
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Concrete Renewable Hydrogen Projects in Development at IPCAR

To be definite we will analyze here three examples of the previously mentioned methodologies which are in development at IPCAR:

- hydrogen production by thermal –solar water splitting with quantum boost.
- hydrogen production by plasma torch gasification
- hydrogen production by ethanol steam reforming and partial oxidation

Hydrogen Production by Water Splitting

Hydrogen production by water splitting is developed around the project entitled “Solar Water Splitting with Quantum Boost”. This process was conceived by a team composed of researchers from: Science Applications International Corporation (SAIC), San Diego, CA, the Florida Solar Energy Center at University of Central Florida (FSEC-UCF), Cocoa Beach, FL with a modest collaboration of IPCAR at UT. This project was awarded by the Department of Energy

Water Splitting Process with Quantum Boost

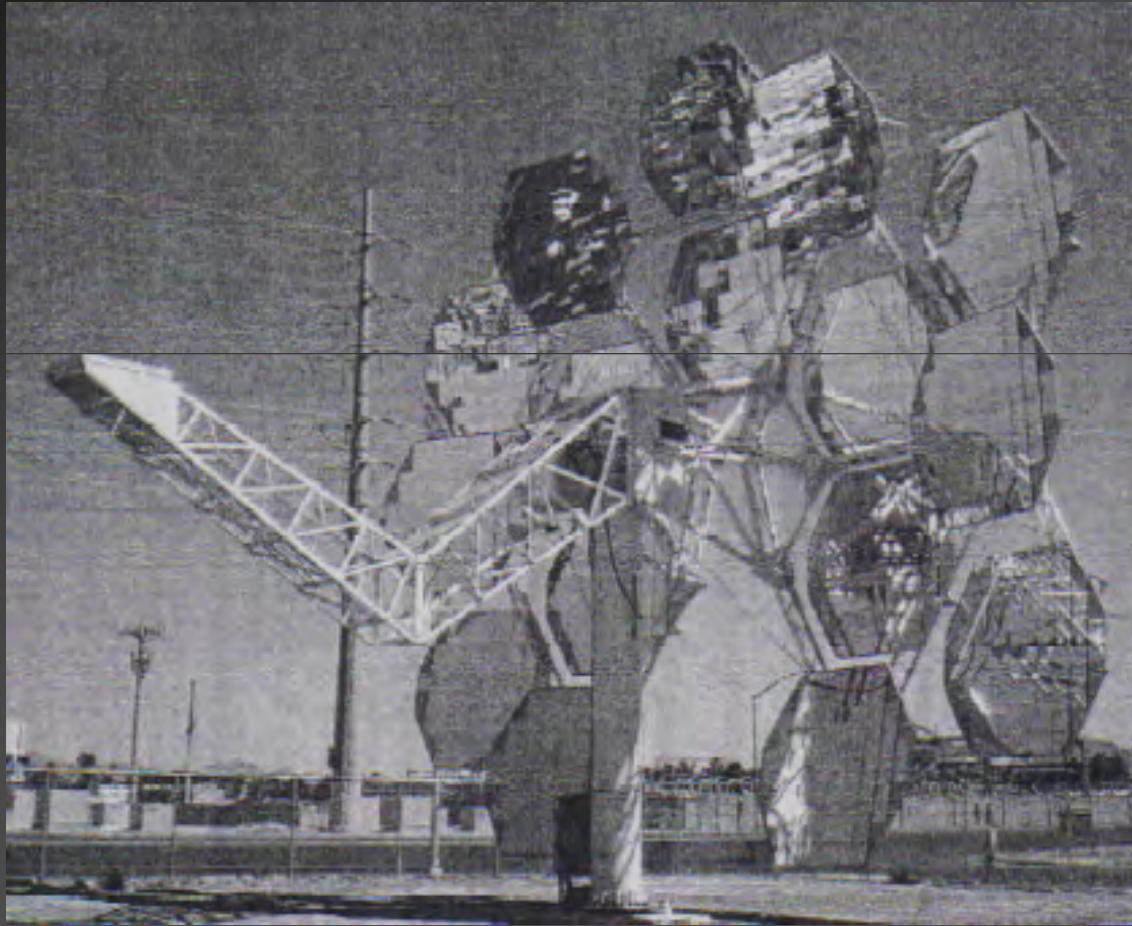
The approach is based on splitting water using a two-step high-temperature cycle which includes one step utilizing solar (visible and/or near-UV) photons according to the following scheme [6]:



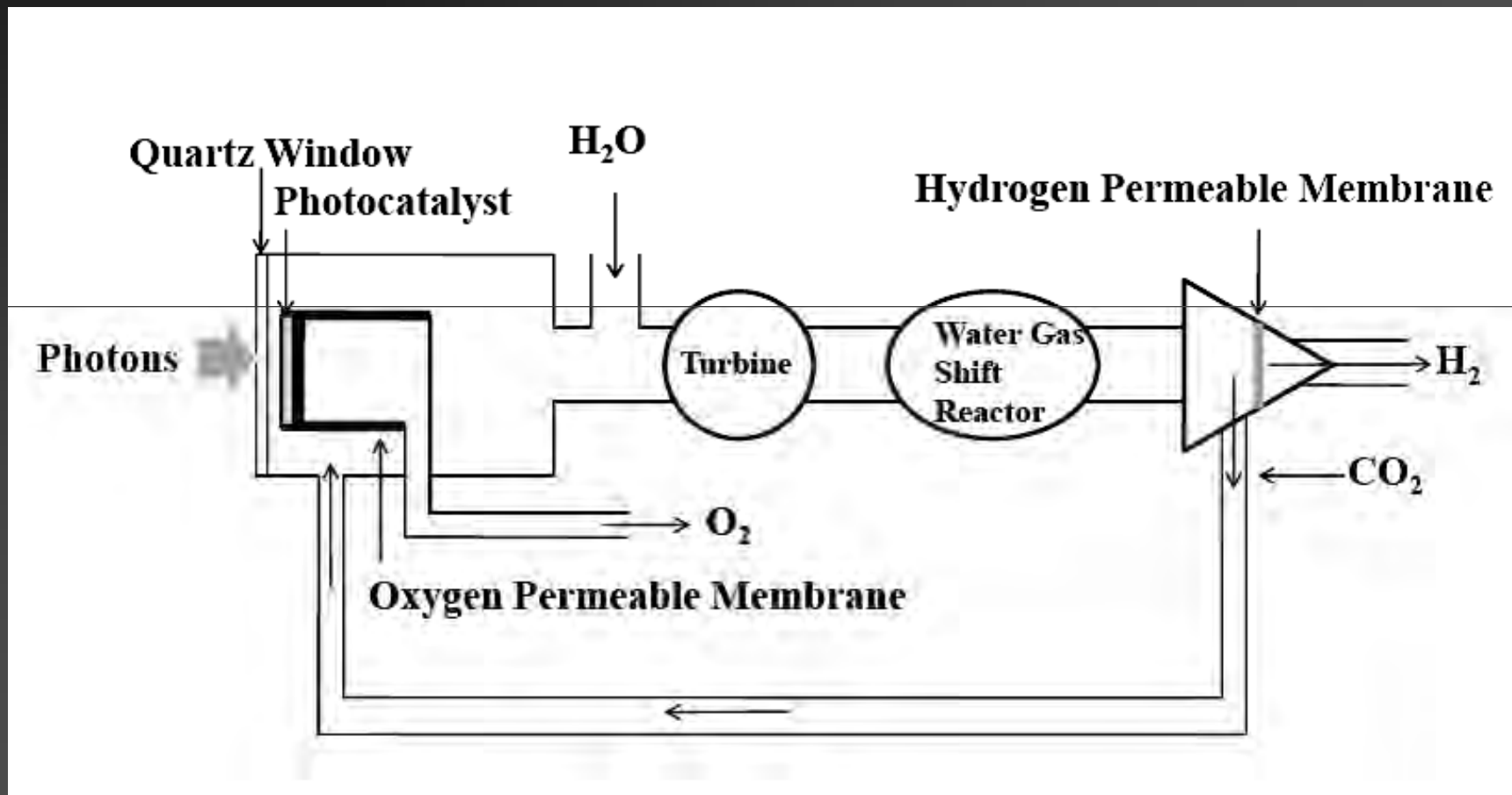
CO₂ Cycle for Water Splitting with Quantum Boost

The energy requirement for the dissociation reaction is more propitious in the case of CO₂ than for water, since reaction “1” has a larger thermal, $T\Delta S$, component of the total energy, ΔH , than the water dissociation reaction. Second, at high temperatures, that is, larger than 1500 K, CO₂ becomes susceptible to near-UV and even visible light absorption. This results in CO₂ thermal dissociation at a temperature range between 2000-2500 K. A span readily achievable in state-of-the-art solar concentrators such as those developed by SAIC [6]

SAIC Dish Concentrator System



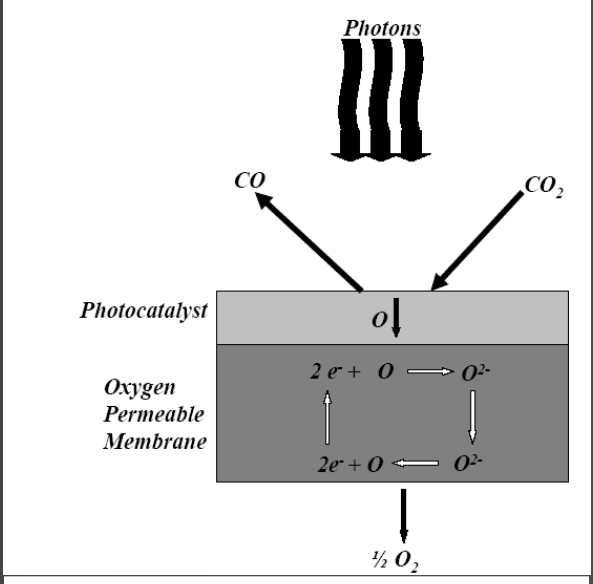
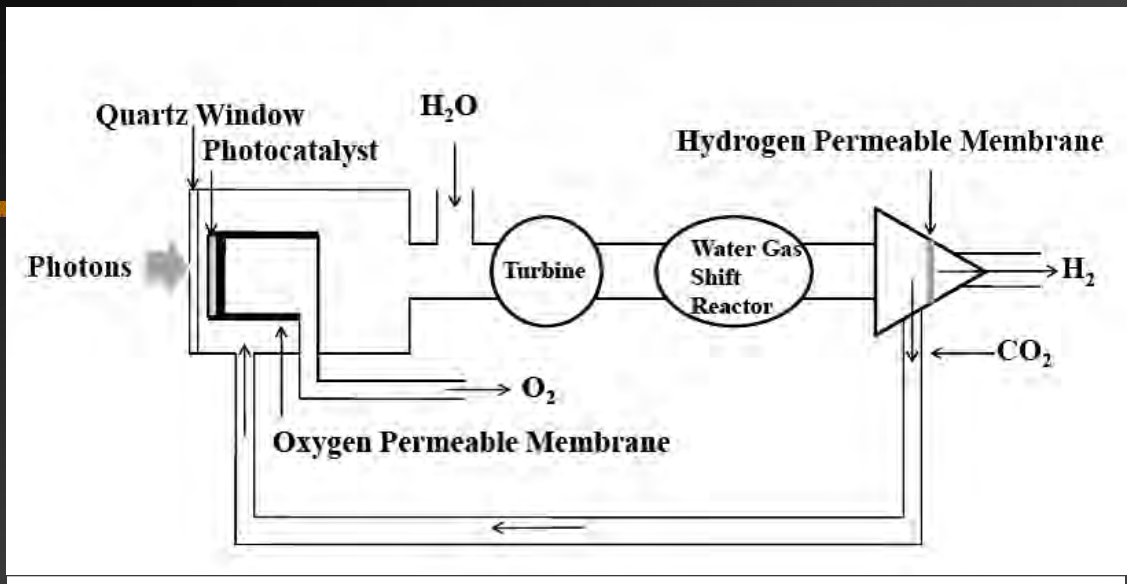
Schematic Diagram Describing the Solar-powered Process for High-temperature Water Splitting [6]



Membranes

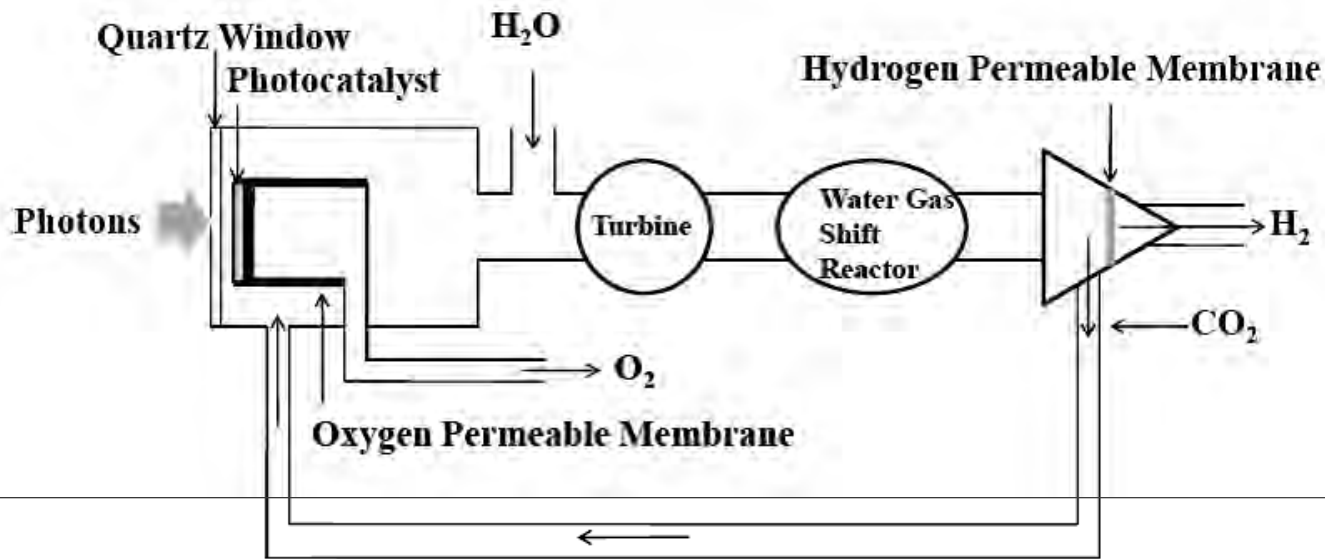
A membrane is a perm-selective barrier between two phases capable of being permeated due to a driving force, that is pressure, concentration or electric field [7]

First Step: $\text{CO}_2 + \text{heat}/h\nu \rightarrow \text{CO} + \frac{1}{2} \text{O}_2$



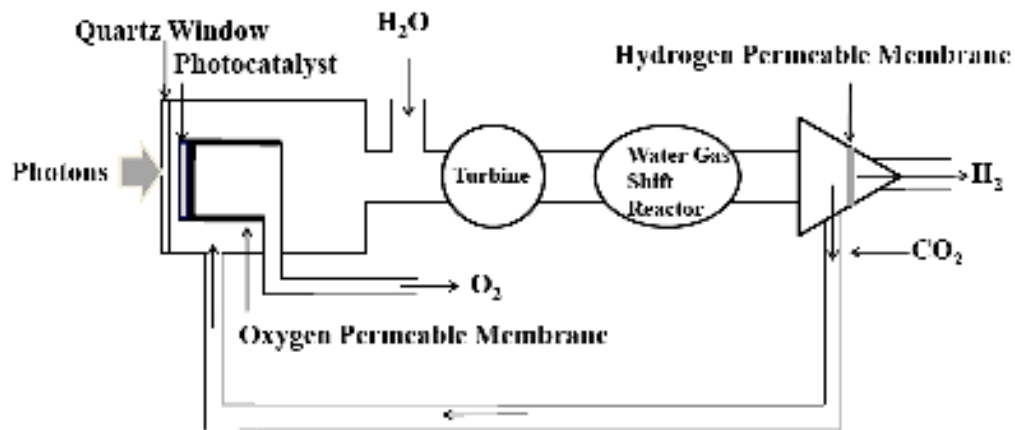
The directly irradiated solar reactor is exposed to concentrated solar radiation through the quartz window. Then, the photocatalyst enhances the kinetics of the CO_2 dissociation via an interaction with the active sites, leading to weakening of $\text{C} = \text{O}$ bonds [6]. In addition, the ceramic oxygen-permeable membrane further accelerates the process of CO_2 decomposition by shifting the reaction equilibrium towards oxygen production by the withdrawal of oxygen from the reaction chamber.

Phase 2



The hot gaseous stream leaving the reactor is quenched with water, producing steam that can be used for generating electric power in a turbine; after cooling the effluent to 700 K, the CO-water vapor mixture enters a water-gas shift reactor to produce hydrogen and CO₂ for recycle [6]

Phase 3: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$

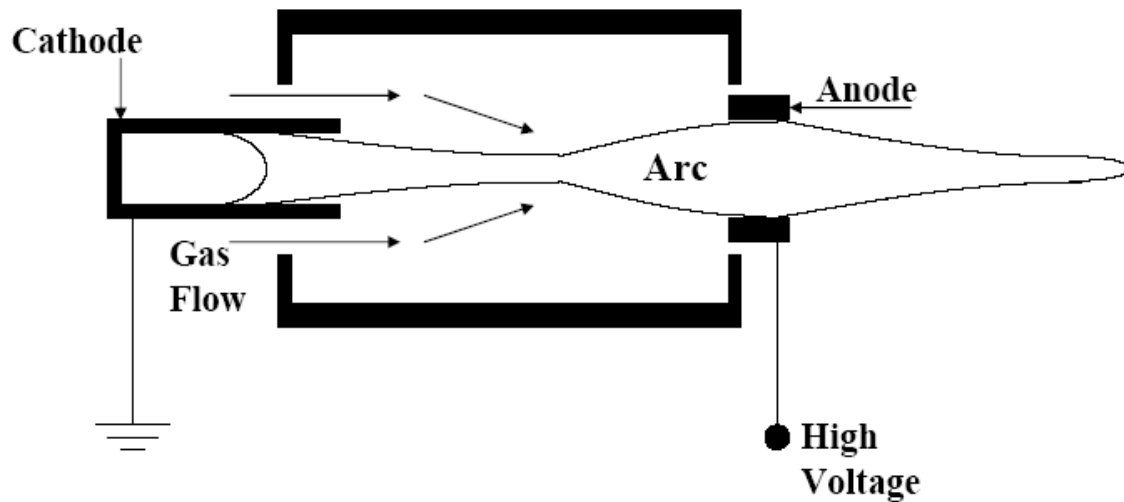


The water-gas shift process (WGS) is applied to maximize CO conversion and H_2 production. It normally proceeds in two stages using Fe_2O_3 structurally promoted with CrO at 300-500 °C for the high temperature shift and $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ at 200-250 °C for the low temperature shift [5]. Then, after cooling CO-water vapor mixture down to 500 °C, it passes through the water-gas shift reactor to generate hydrogen and CO_2 . The hydrogen- CO_2 mixture is separated by means of a hydrogen-permeable membrane producing high purity hydrogen and CO_2 for recycle [6]

Hydrogen Production by Solid Waste Plasma Thermal Gasification

Thermal gasification is the chemical conversion, at high temperatures, of compounds containing organic and inorganic components into: a combustible gas mixture (the organic part) and the inorganic component in a glassy material. Specifically, thermal gasification with a plasma torch, dissociates virtually all forms of organic compounds, and melts everything that is not organic, because of the extremely high temperature at which the process takes place

Plasma Torch



The plasma torch is a device applied for the production of plasma at atmospheric pressure and temperatures bigger than $5,000^{\circ}\text{C}$

Plasma is the ionized state of matter, which is composed by a gas of charged and neutral particles, formed when ordinary matter is heated over $5,000^{\circ}\text{C}$

The torch create a plasma by the formation of an electric arch between the anode and the cathode. The arc is produced by the electric breakdown of the flowing gas which generates an electric current which allows the transference of energy to the formed plasma by accelerating the charged particles in the electric field

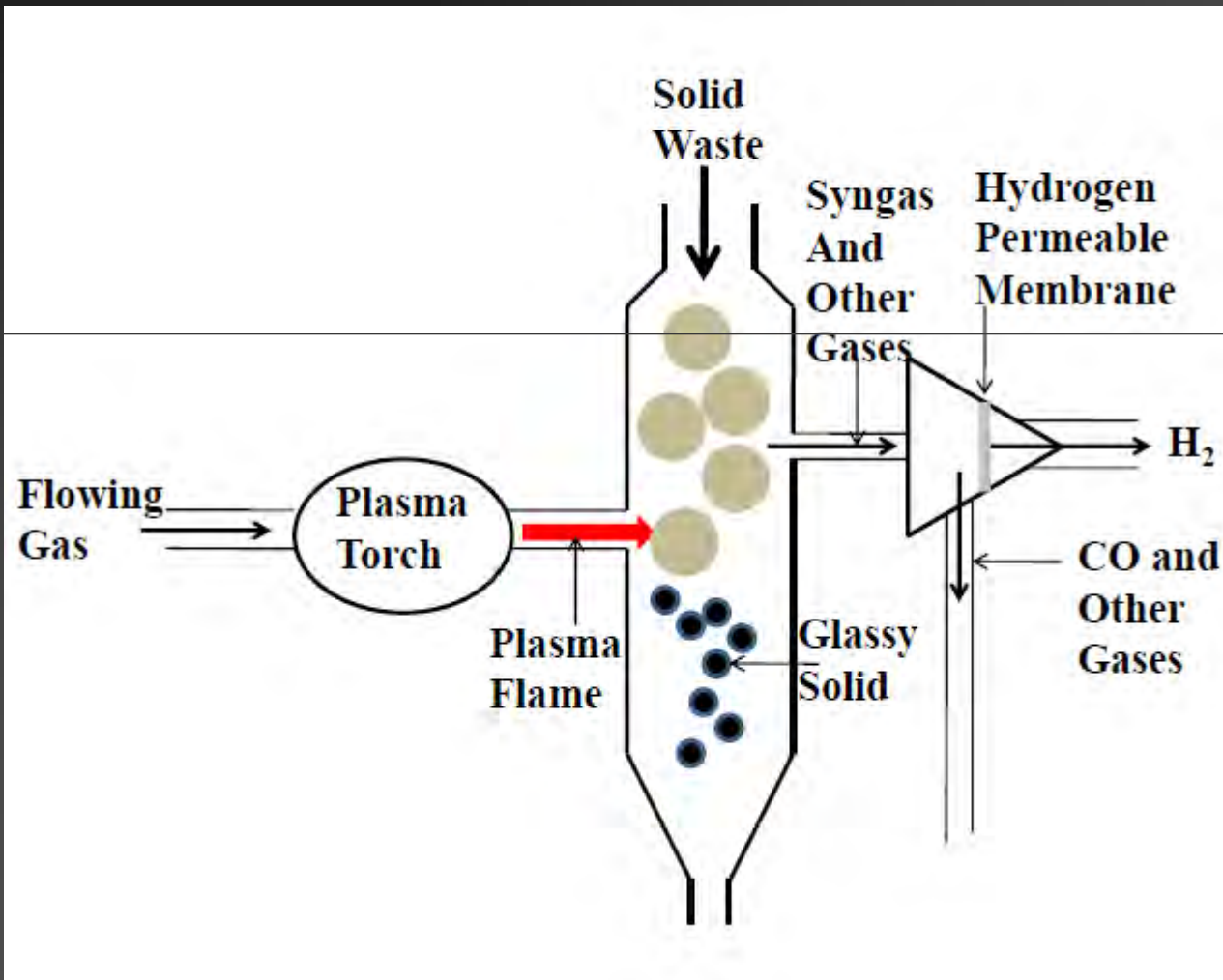
Plasma Torch Gasification of Solid Waste

The plasma torch gasification methodology allows the dissociation of the organic component of the solid waste; producing, from all the organic components of the solid waste, only simple molecules, such as: CO and H₂ (syngas) and other simple molecules like: H₂O, CO₂, N₂ and CH₄; given that, only these molecules resist the high temperatures within the plasma, without dissociation

Plasma Torch Vitrification of Solid Waste

Additionally it is produced the vitrification of the inorganic component of the waste. In other words: the outcome of the interaction between plasma and the inorganic materials contained in the solid waste is a glassy solid

Scheme of the Facility to Produce Hydrogen by Plasma Torch Gasification



Hydrogen Production by Ethanol Steam Reforming and Partial Oxidation

As was previously commented, one of the major uses of hydrogen will be transportation. However, since hydrogen is highly unstable; it is possible to safely produce it, in situ, in order to feed a converting device such as a fuel cell. In this regard, ethanol is an excellent aspirant

Ethanol

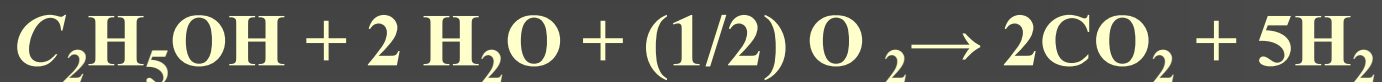
Ethanol (C_2H_5OH) a natural product produced, normally, by yeast fermentation of sugars, is a renewable, available, easily transportable, biodegradable and a low toxicity source of energy, which can be manufactured with food biomass and also with non food biomass

Ethanol Steam Reforming Plus Partial Oxidation

The overall endothermic steam reforming reaction of ethanol can be represented as follows:



In the case where oxygen is added the following exothermic reaction describes the process:



These are apparently simple reactions; however, are impossible without a catalyst. The appropriate catalysts are normally transition metals supported in acid high specific surface area materials

Why In Situ Ethanol Steaming plus Partial Oxidation?

The complete advantages of the hydrogen economy are only accomplished when hydrogen is produced from renewable resources such as non-food biomass. Thus, ethanol reforming plus partial oxidation can be the basis for the use of ethanol for renewable hydrogen production. Since, ethanol, is an excellent hydrogen carrier, without the disadvantages associated with hydrogen storage, transportation and safety issues.

Why Appropriate Catalysts?

There are many reaction pathways that can occur in the ethanol steam reforming plus partial oxidation. process depending on the applied catalysts. As a result, a big effort is necessary to obtain an active, selective and long-lasting catalyst to develop a procedure for hydrogen production by ethanol steaming and partial oxidation.

Catalysts Activity

The catalyst activity is related with the increment in the reaction rate [5]. The application of bifunctional zeolites and mixtures of acid zeolites and carbon-nanotubes with supported Ni and Pd nanoparticles is our approach to get an active catalyst

Catalysts Selectivity

Selectivity, means high yield of a particular product, i.e., the capacity of the catalyst to conduct the conversion of the reactants in one particular way path [5]. In the present case this is the most important issue. The application of bifunctional zeolites and mixtures of acid zeolites and carbon-nanotubes with supported Ni and Pd nanoparticles is our approach to get a selective catalyst

Zeolites and Carbon Nanotubes

Zeolites and carbon nanotubes, because of its: surface chemistry properties, controlled porosity, high specific surface area, stability at relatively high temperature and simplicity of the synthesis process, are among the most promising base materials to support transition metal nanoparticles to produce catalysts. These materials have not been studied as catalyst of the ethanol steam reforming plus partial oxidation reaction. Consequently, its test, is a rational choice

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