University of **C**hemical **T**echnology and **M**etallurgy

Center for Hydrogen Technology

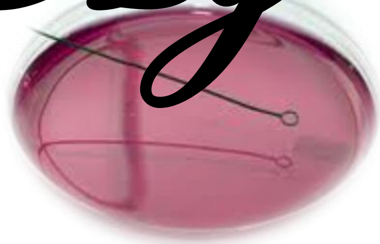
Sofia,**Bulgaria**

An Innovation Week on R.E.S.

Hy^2 *Divices*

4 Solution

Innovation and Abilities



Hybrid System for Bio-Hydrogen Production

eng. Elitsa Petkucheva

(Student)

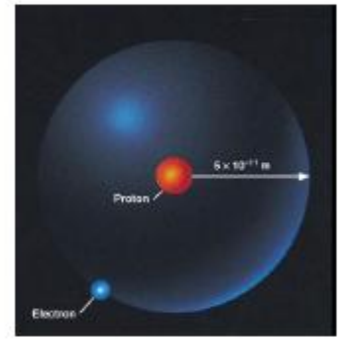
Hydrogen Economy

Why is new energy needed?

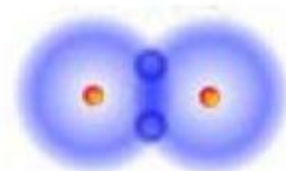
- Population Growth
- Development on Rest of World
- Energy Consumption Forecasts
- Energy Reserves Forecasts

Hydrogen Characteristics

- Discovered by Henry Cavendish 1776

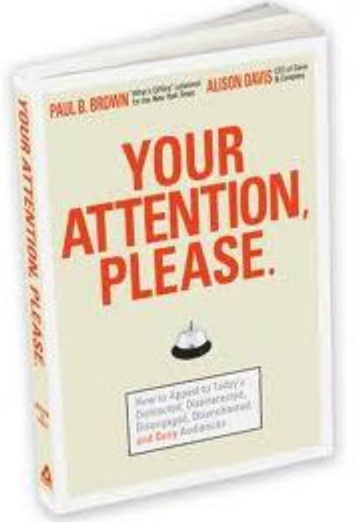


- Smallest element – one proton, one electron
- Stable molecule is H_2



- 2 hydrogen, 1 oxygen = water

- 14 times lighter than air, 8 times lighter than natural gas
- 3 times more energy/pound than gasoline or diesel
- But 6% energy/volume at 170 bar as gasoline (big tanks)



Why Hydrogen?

Not liquid or gaseous form of dynamite !!!

Advantages

>Colorless

>Odorless

>Nontoxic

>Does not produce acid rain

>Does not deplete ozone

>When pure Hydrogen is used in a fuel cell the products are electricity, heat and water

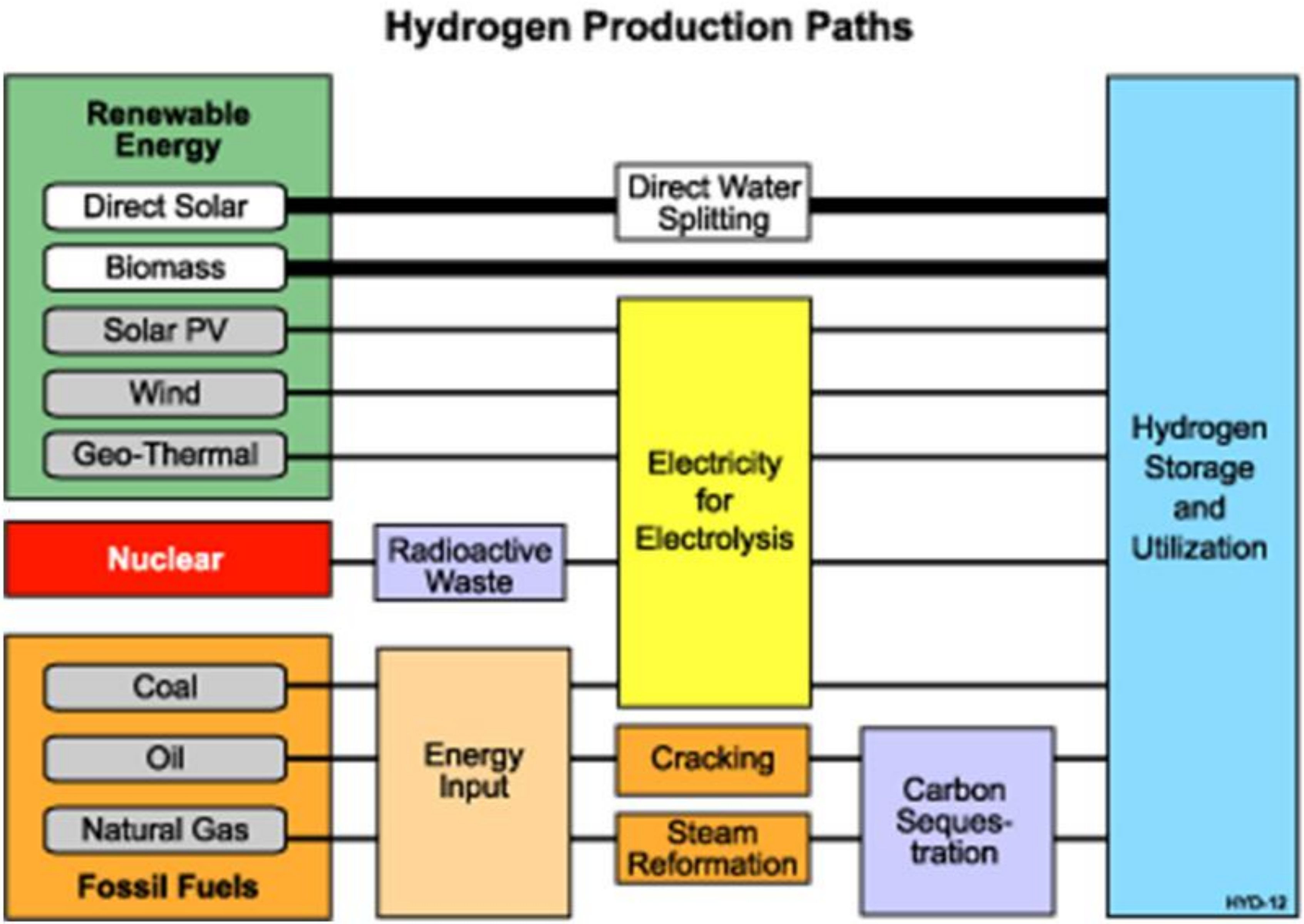
Disadvantages

>**Burns vs. Explodes**

>1/10 the heat of gas fire

>22 x weaker than gas explosion at the same explosion

>No smoke

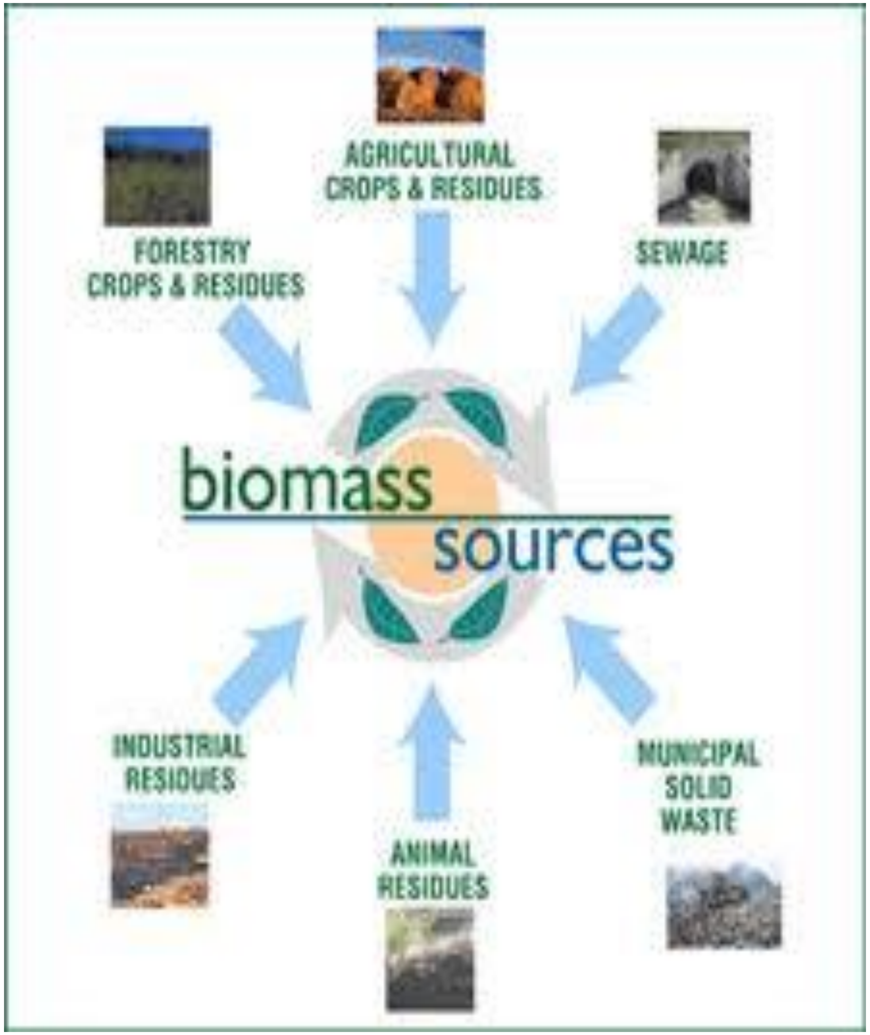

Hydrogen Production Paths
Renewable Energy
Direct Solar
Biomass
Solar PV
Wind
Geo-Thermal
Direct Water Splitting
Electricity for Electrolysis
Nuclear
Radioactive Waste
Coal
Oil
Natural Gas
Fossil Fuels
Energy Input
Cracking
Steam Reformation
Carbon Seques-tration
Hydrogen Storage and Utilization
HYD-12

Waste Water



Wastewater, also spelled waste water, is any water that has been adversely affected in quality by anthropogenic influence. It comprises liquid waste discharged by domestic residences, commercial properties, industry, and/or agriculture and can encompass a wide range of potential contaminants and concentrations.

Biomass

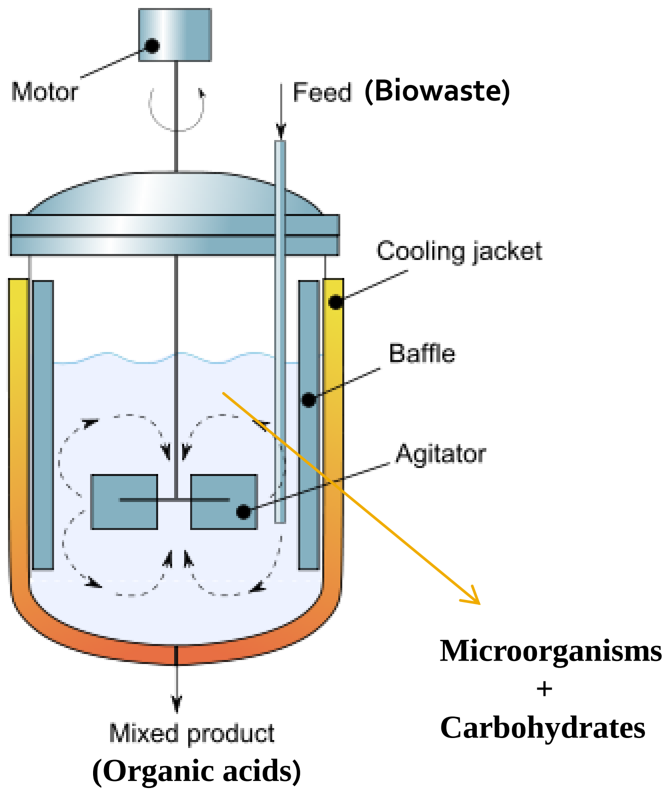


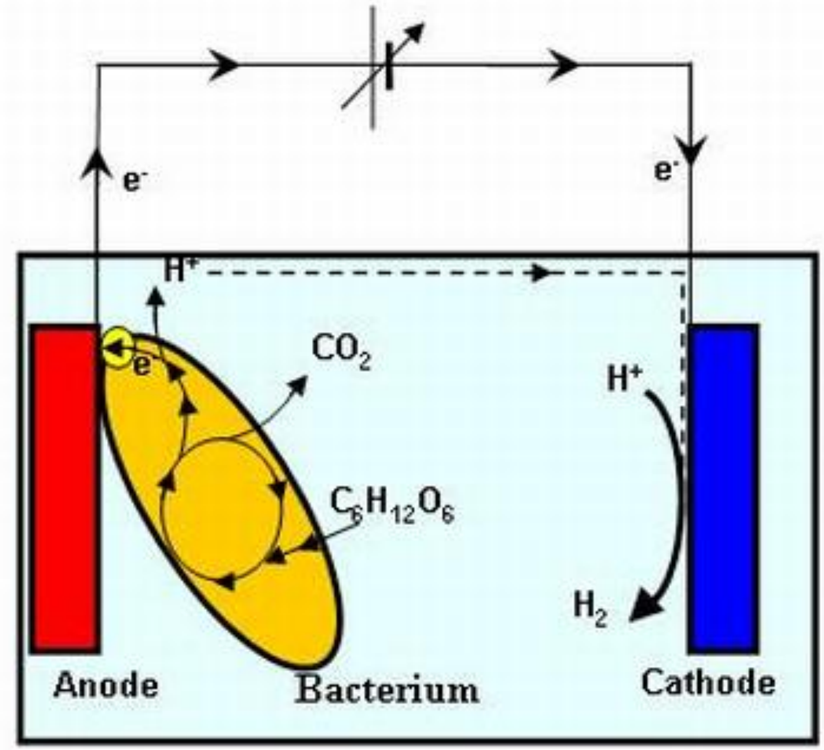
Biomass, as a renewable energy source, is biological material from living, or recently living organisms

Industrial biomass can be grown from numerous types of plants, including miscanthus, switchgrass, hemp, corn, poplar, willow, sorghum, sugarcane,and a variety of tree species, ranging from eucalyptus to oil palm (palm oil).

Biomass is carbon, hydrogen and oxygen based.

Compartments and Mechanisms at work





Continuously Stirred Tank Reactor
(Dark Fermentation)

Membrane-Free Microbial Electrolysis Cell
(Carbon Fixation and Electrohydrogenesis)

Main Processes

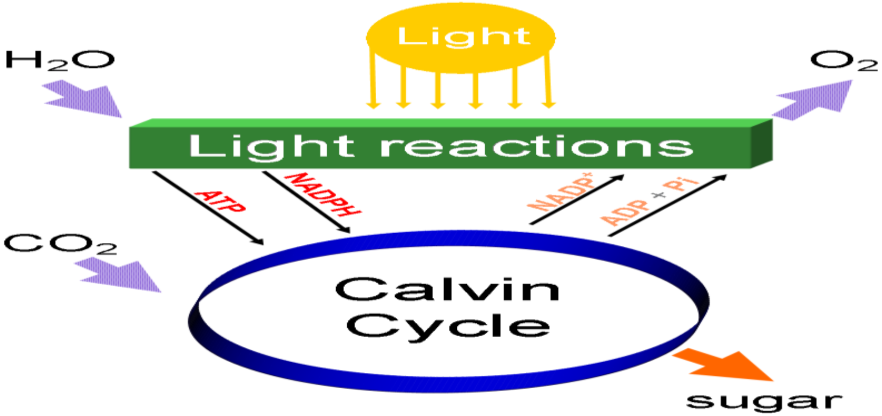
Dark Fermentation:

$$C_6H_{12}O_6 + 4H_2O \rightarrow 2CH_3COO^- + 2HCO_3^- + 4H^+ + 4H_2$$
$$\Delta G^o = -206.3 \text{ kJ mol}^{-1} \quad (1)$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COO^- + 2HCOO^- + 4H^+ + 2H_2$$
$$\Delta G^o = -209.1 \text{ kJ mol}^{-1} \quad (2a)$$

$$2HCOOH \rightarrow 2CO_2 + 2H_2$$
$$\Delta G^o = -6 \text{ kJ mol}^{-1} \quad (2b)$$

Carbon fixation:



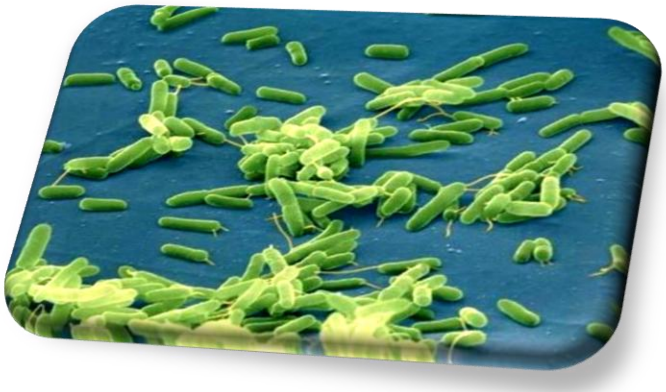
Microbial electrolysis:

Anode: $C_2H_4O_2 + 2\ H_2O \rightarrow 2\ CO_2 + 8\ e^- + 8\ H^+$

Cathode: $8\ H^+ + 8\ e^- \rightarrow 4\ H_2$

Used Microorganism

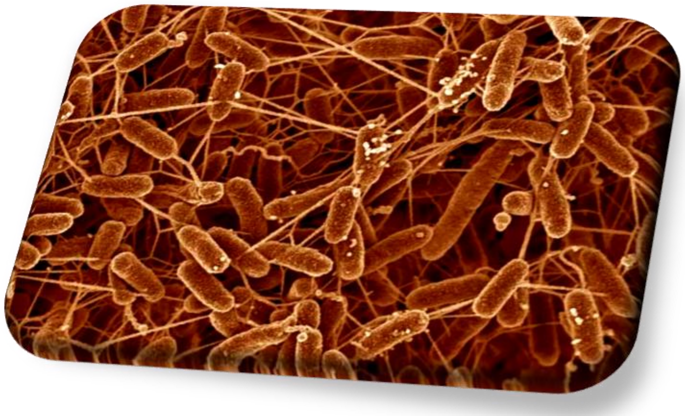
Dark Fermentation



Caldicellulosiruptor saccharolyticus

- thermophilic (70° C)
- strictly anaerobic asporogenous bacterium
- it hydrolyses a variety of polymeric *carbohydrates* (cellulose, hemicellulose, pectin, a -glucan (starch, glycogen), *b -glucan* (lichenan, laminarin), guar gum) to acetate, lactate, hydrogen and CO 2
- high yield and low product inhibition
- simultaneous utilisation of sugars (cellulose, hemicellulose, pectin)
- growth at elevated temperatures: robust thermophilic organisms, with a decreased risk of contamination.

Carbon Fixation and Electrohydrogenesis



Shewanella oneidensis MR-1

- reduce poisonous heavy metal and can live in both environments with or without oxygen
- proteobacterium
- facultative bacterium, capable of surviving and proliferating in both aerobic and anaerobic conditions
- known as "Dissimilatory Metal Reducing Bacteria (DMRB)" because of their ability to couple metal reduction with their metabolism
- Fixed CO2
- produce long chain hydrocarbons directly from carbon dioxide, water and sunlight

Mechanisms for electron transport to electrodes

A. Indirect electron transport by reduced products

Reduced products of microbial fermentation were abiotically oxidized at the anode surface to provide electrons.

B. Electron transport by artificial mediators

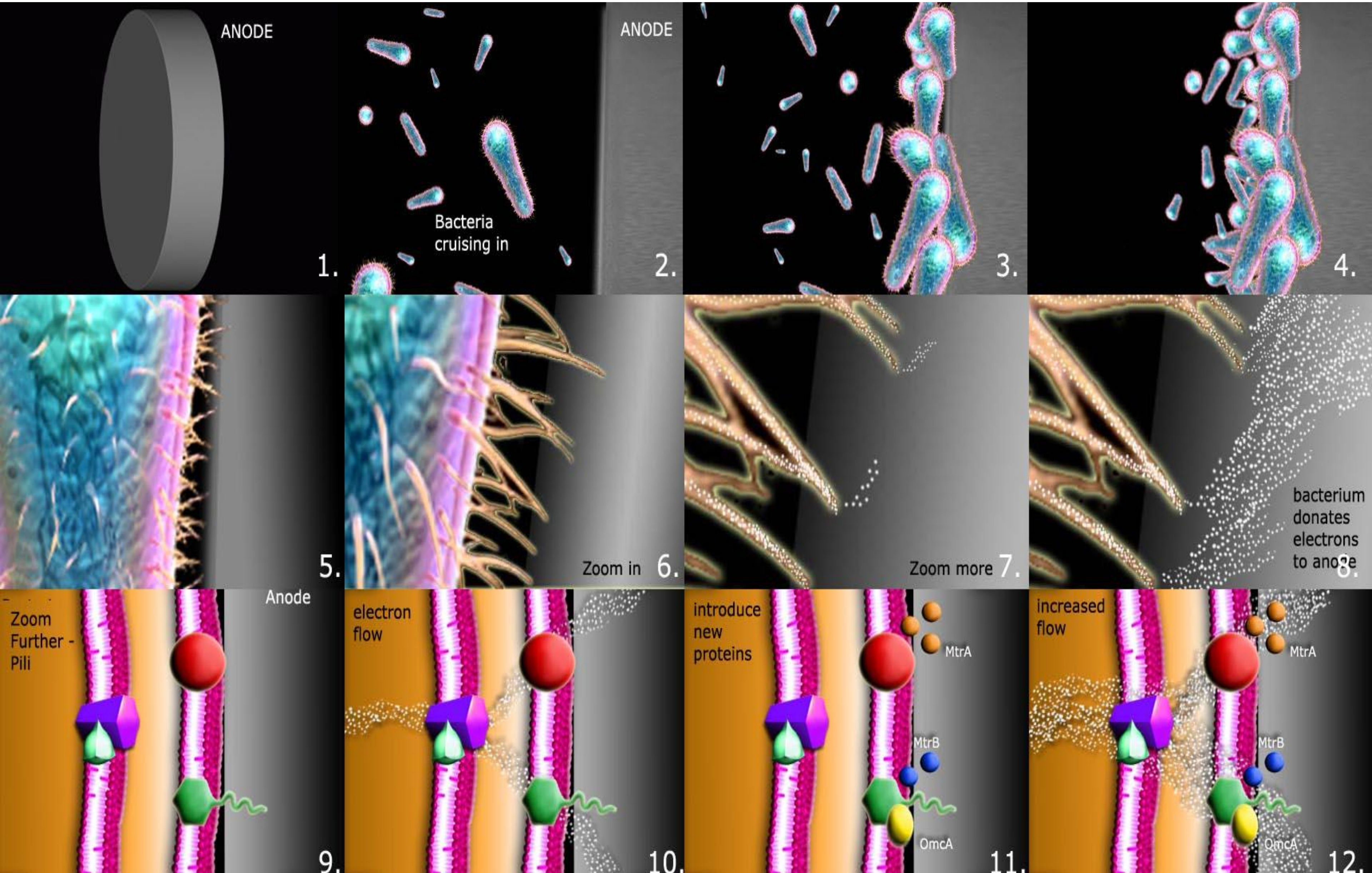
In this proposed mechanism electrons are transported by artificial mediators, sometimes referred to as electron shuttles .This chemical materials offer the possibility for microorganisms to generate reduced products that are more electrochemically active than most fermentation products.

C. Electron transport through microorganism’s own mediator

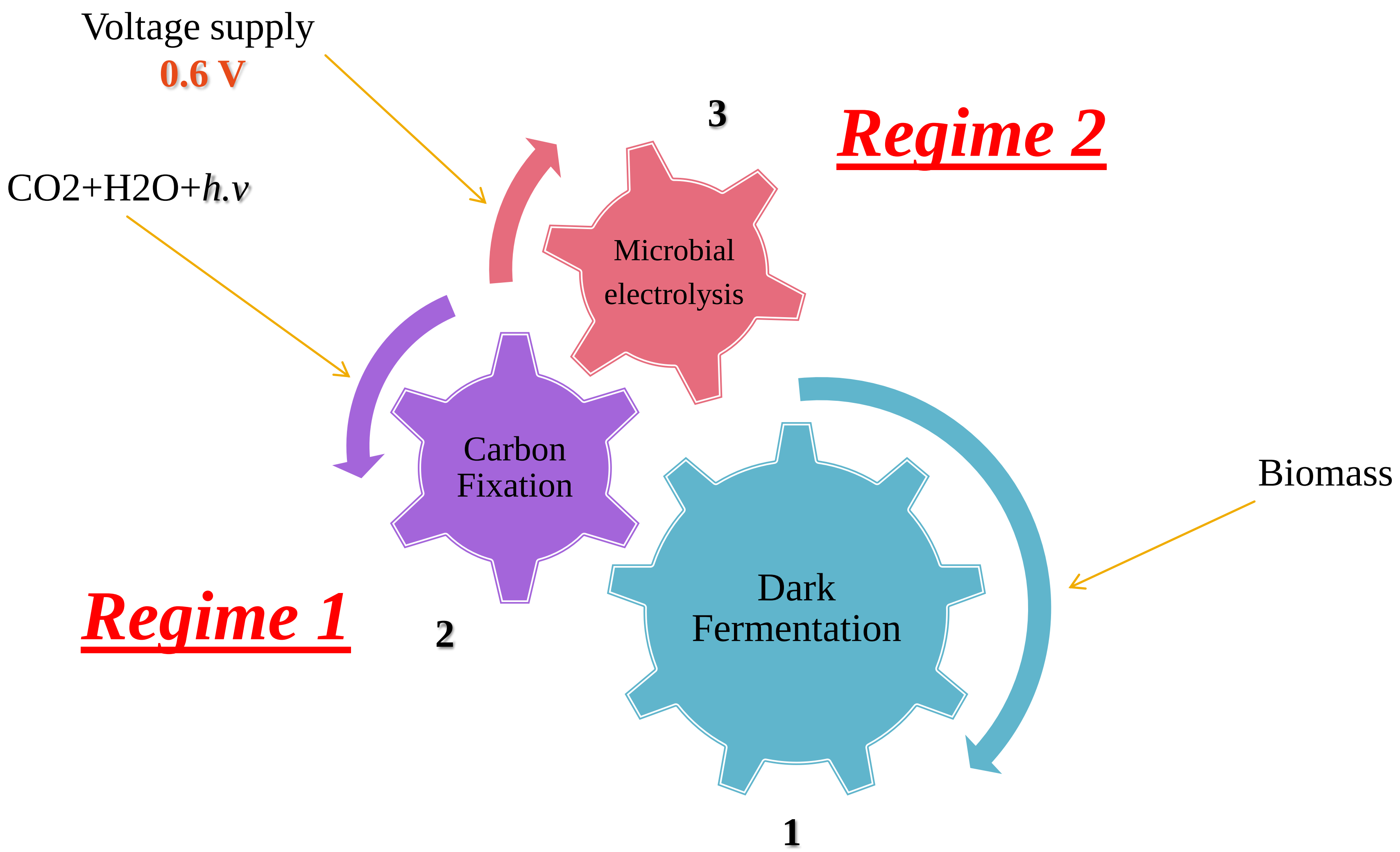
It is also known that some microorganisms can produce their own mediators to promote extracellular electron transfer.

D. Direct electron transfer

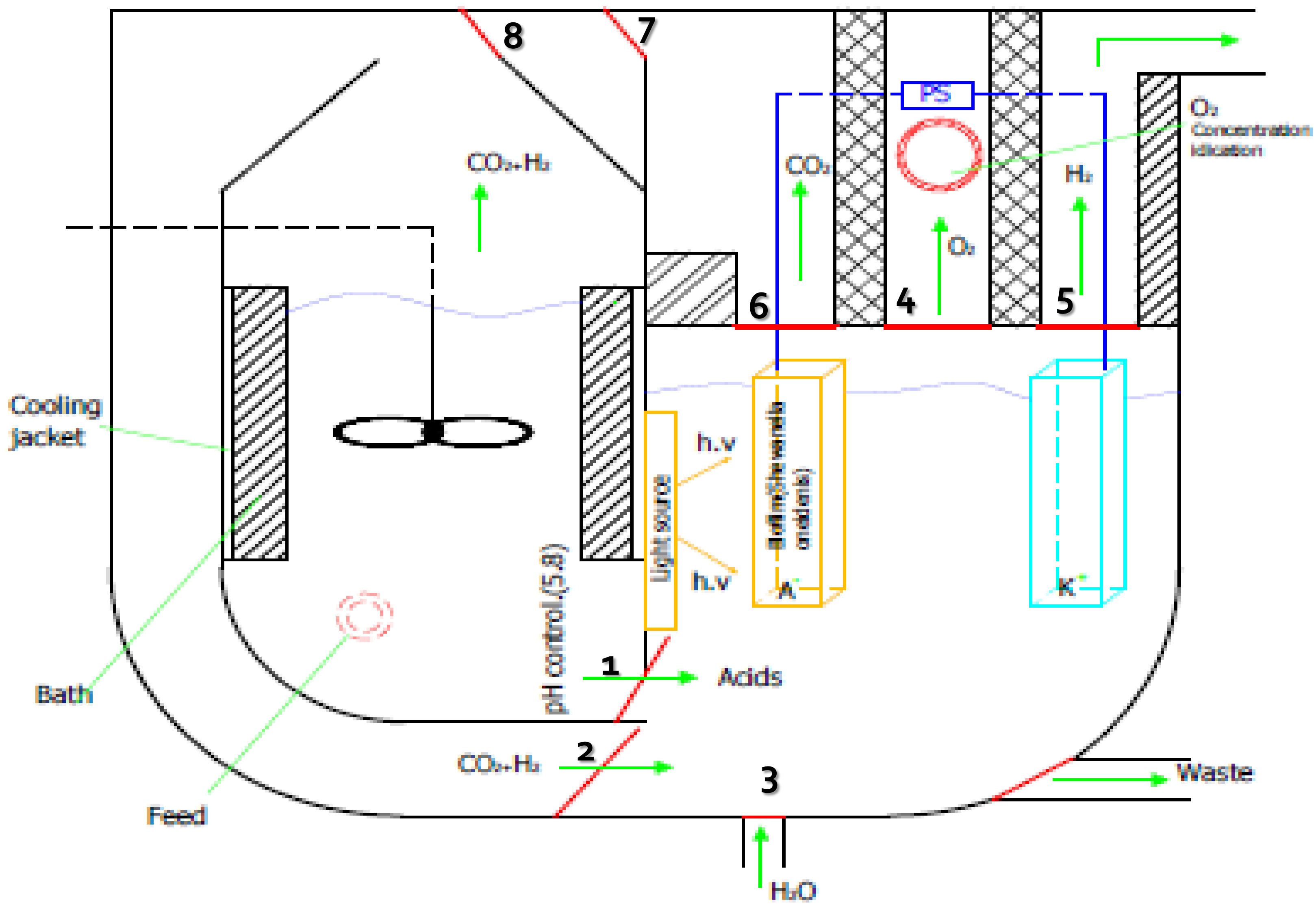
Nanowires formation and Electron transportation by Shewanella Oneidensis MR-1



Sequence of processes

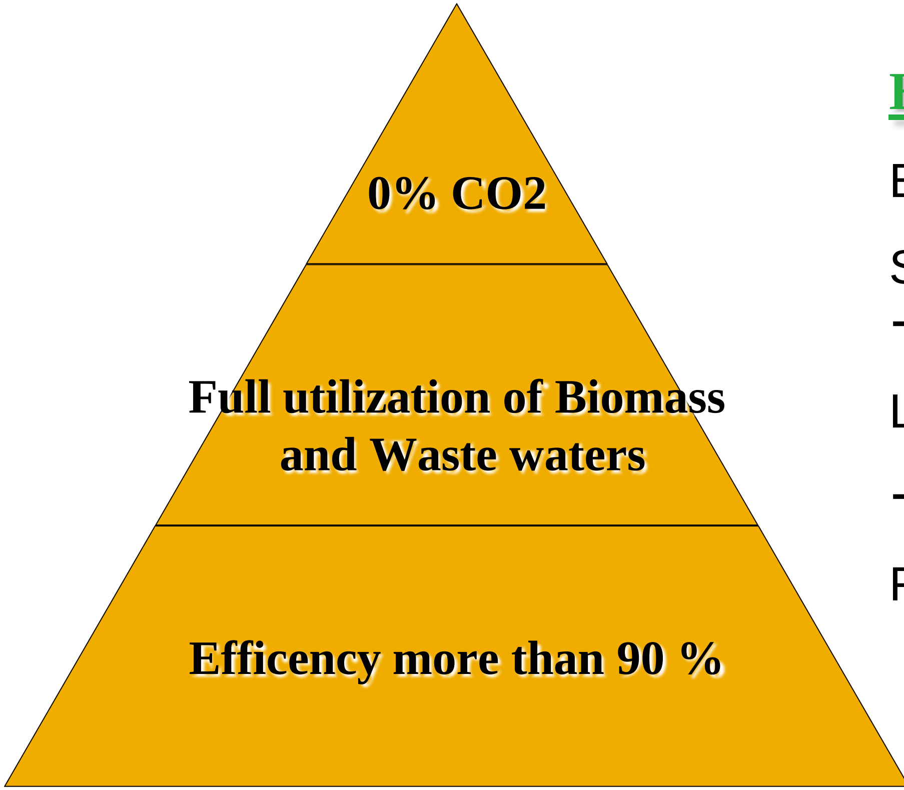


Design



8
7
CO_2+H_2
CO_2
PS
O_2
Concentration idication
H_2
O_2
6
4
5
Cooling jacket
pH control (5.8)
Light source
h.v
h.v
A
K
1
Acids
Bath
2
CO_2+H_2
3
Waste
Feed
H_2O

Calculations and Numbers



Hydrogen productivity per mol substrate:

Ethanol: $CH_3CH_2OH + 3H_2O \rightarrow 6H_2 + 2CO_2$

Succinic acid: $COHCH_2CH_2COOH + 4H_2O \rightarrow 7H_2 + 4CO_2$

Lactic acid: $CH_3CHOHCOOH + 3H_2O$

$\rightarrow 6H_2 + 3CO_2$

Formic acid: $HCOOH \rightarrow H_2 + CO_2$

1,8 tones CO_2 → 1 tones Biomass → 57 kg H_2

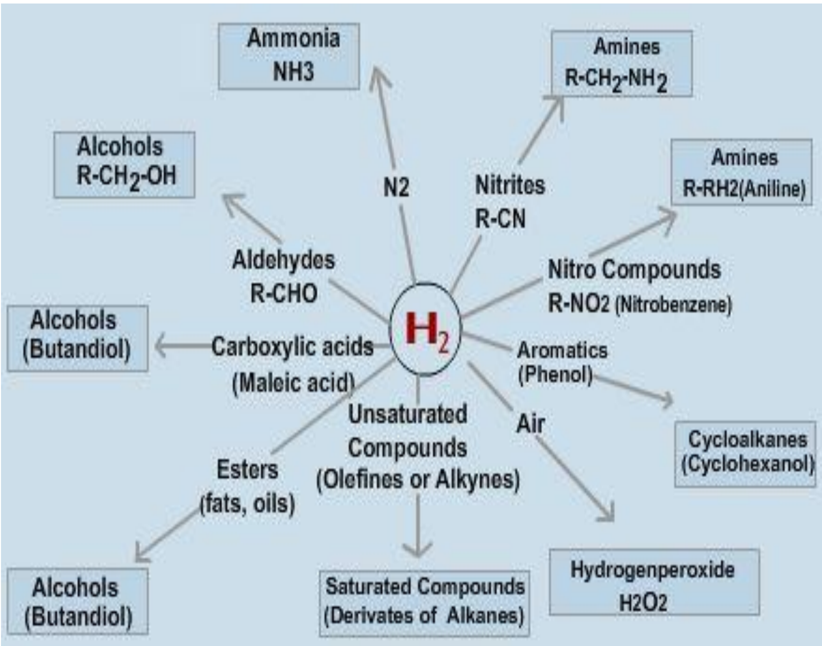
Calculations and Numbers

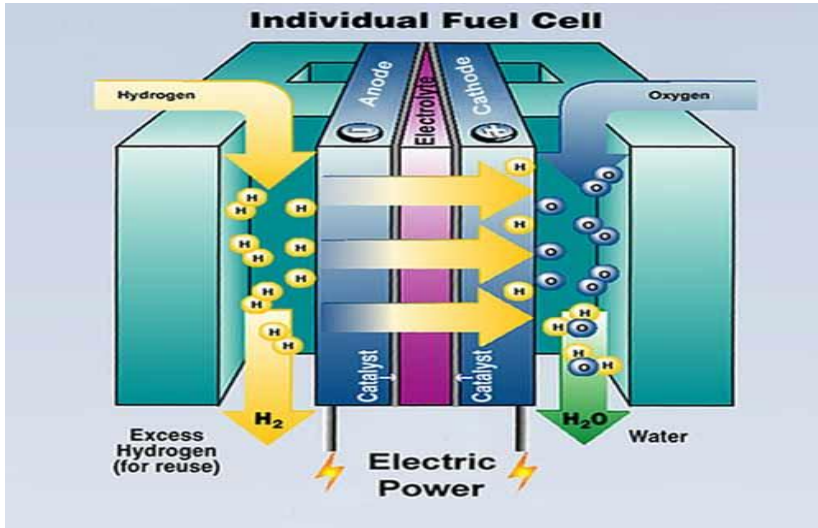
Voltage (V)	Current Density (A/m^2)	pH	H_2 production Rate $(m^3/day/m^2)$
0.6	9.3	7	0.11
0.6	14	5.8	0.15

Pros

✓Higher rates of Hydrogen recovery(**more than 90% of Hydrogen can be harvested**)
✓Ability to use more diverse substrate
✓**No Carbon dioxide emissions**
✓Eliminating the requirement for expensive catalysts on the anode and the potential achievement of simultanious waste reduction
✓Reduction of the production area
✓**Easy to operate**

Hydrogen applications





,,A successful innovation policy is one that involves all actors in society , innovation is something you do whit people , not to them"

Jose Manuel Barroso, October 13th 2010

Thank You for your attention.....