

## HYDROGEN ECONOMY FOR TODAY AND TOMORROW

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### ABSTRACT

The technologies of hydrogen production for today and the most promising technologies for the future have been described within this study. All techniques have been evaluated for their environmental impact and the price of the hydrogen that they produce. At the end of our study we suggest according to our evaluation the method for hydrogen production in the future, based on environment impact, cost, and the feasibility of using today's existing systems.

### INTRODUCTION

Fossil fuels have caused many problems on the humanity on the last tow decades. The partial control, of the fossil fuels and especially of petroleum, from a few countries has a significant effect on the rest of the world, particularly on the economy, transports, and on the total cost of living. In addition, the environmental problems from burning of fossil fuels complicate the whole situation. In the early of 20<sup>th</sup> century, scientists have proposed hydrogen as the alternative fuel on the transport as hydrogen has been considered as a "green" fuel. At this period energy demands for transportation was not so high, so hydrogen has not used. Last two decades the one side control of fossil fuels has causes many problems on the economy of many developed countries. So the policy of developed countries was focused on an economy independence from fossil fuels and this could be achieved only by using hydrogen.

Hydrogen has no environmental impact because at the stage of burning generates simply water. Furthermore, as long as hydrogen was produced from biomass the process has no contribution to the environmental pollution. Among the advantages of using hydrogen for energy generation are high value of heating and high value of conversion to electricity via fuel cells. In the past years a great effort has been devoted to investigate alternative routes to produce hydrogen, so today many techniques are available for commercial use. These techniques refer mainly in producing hydrogen from fossil fuels and furthermore from renewable sources such as wind, sun and biomass. Main commercial technique for hydrogen production is steam reforming of methane, as it seems to be the most economical method for the time being. On the other side, this technique has great environmental impact, as it depends from fossil

fuels use, so it seems that it has no future in an economy independent from the fossil fuels.

### TECHNOLOGIES OF TODAY

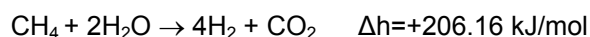
Today's available technologies for production of hydrogen were introduced in this section. Each technology was analyzed with respect to

- the status of the production,
- the environmental impact and
- the cost of produced hydrogen.

### Steam Reforming

Hydrogen is mainly produced by using three major techniques, steam reforming, partial oxidation and electrolysis. Over 90% of hydrogen is manufactured by steam reforming of methane (SMR).

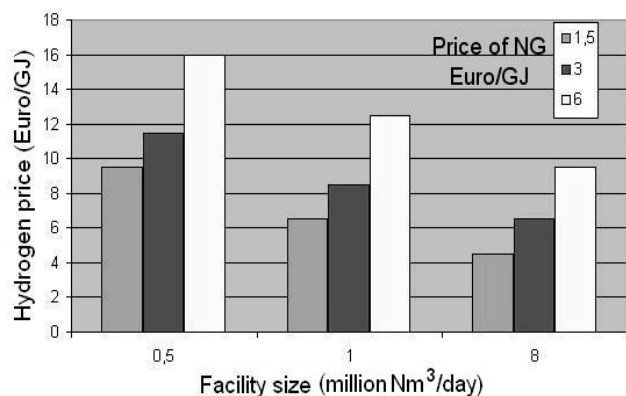
Hydrogen production from Natural Gas is accomplished in several steps: desulfurisation of NG, pre-reforming, steam reforming, water gas shift reaction and hydrogen purification. The SMR reaction



is highly endothermic and requires external heat input. Commercial reactors operate at temperature values ranging from 700°C to 800°C and pressure values from 3 to 20 atm. Water gas shift reaction very often has been accomplished in two stages. In the first stage, reactor operates at temperatures about 350°C – 475°C and high degree of conversion has been accomplished, while in the second stage reactor operates at temperatures about 200°C – 250°C and shift reaction was completed with low CO formation. The required heat for the reaction usually comes by burning of NG.

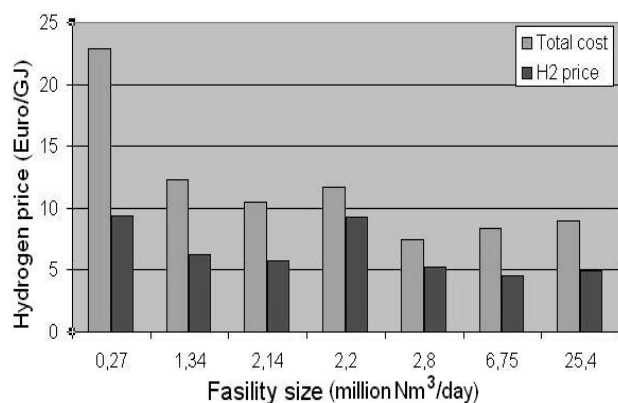
This method is used in developed countries and as long as cost of NG is relatively low, otherwise hydrogen is produced by partial oxidation of heavy hydrocarbons. Typical efficiency of commercial reactors is 70 up to 80%. The cost of hydrogen with this method is about 4,5 – 9,3€/GJ.

The final prices of hydrogen were affected mostly from the size of production unit, so larger units have low operating cost and therefore the price of hydrogen is in this case rather low. The cost of NG in hydrogen price was estimated at about 52% -68%.



**Figure 1.** Cost of H<sub>2</sub> as function of facility size and cost of NG for SMR reaction

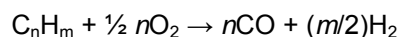
This technique has two disadvantages; the first one is the CO<sub>2</sub> production and the second one is the dependence of hydrogen production on fossil fuels, the latter has straight effect on hydrogen price. These disadvantages may have great affect in the possible future expansion of this technique for an economy based on hydrogen.



**Figure 2.** Cost of H<sub>2</sub> as function of facility size (SMR)

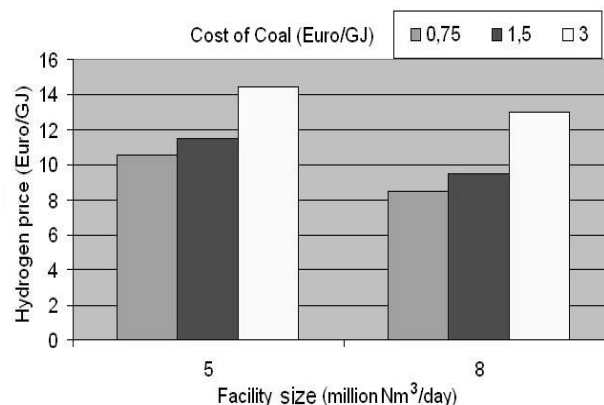
### Partial Oxidation

Partial oxidation (POX) technique is used for hydrogen production from a) coal b) methane c) heavy hydrocarbons. The general partial oxidation reaction is



and it has been applied to all hydrocarbon and coal. Coal is needed pre-treatment before goes into the POX reactor. The pre-treatment include grinding of coke, following by water dissolution.

The partial oxidation reaction of heavy hydrocarbons and coal are used in developing countries, as the price of NG is very high or this is not available at all. Partial oxidation efficiency of coal is 45 up to 50%, efficiency of POX heavy hydrocarbon is about 70%. Final prices of H<sub>2</sub> from POX of coal is 5,8€/GJ up to 15,2€/GJ depends on purity and cost of feedstock.

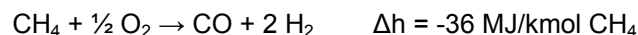
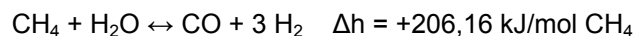


**Figure 3.** Cost of H<sub>2</sub> as function of facility size and cost of coal for POX reaction

The cost of POX procedure for heavy hydrocarbons (petroleum) is higher than the one for coal, because for heavy hydrocarbons more expensive equipments are needed. The hydrogen production by partial oxidation reaction seems to have two disadvantages, environmental and economic a) CO<sub>2</sub> production and b) hydrogen production dependence on fossil fuels. This could cause problems in a possible future economy based on hydrogen and being friendly to the environment.

### Autothermal reforming

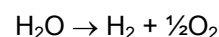
This technique is a combination of steam reforming and partial oxidation. Main fuel for hydrogen manufacture is methane. The reactions



are exothermic and endothermic, respectively. The reactor doesn't need any external heat, as thermal equilibrium has been reached within two reactions. This technique has been used in small reformers and mainly for mobile applications.

### Electrolysis of water

Electrolysis of water is the first technique that has ever been used for hydrogen production. The reaction of electrolysis is

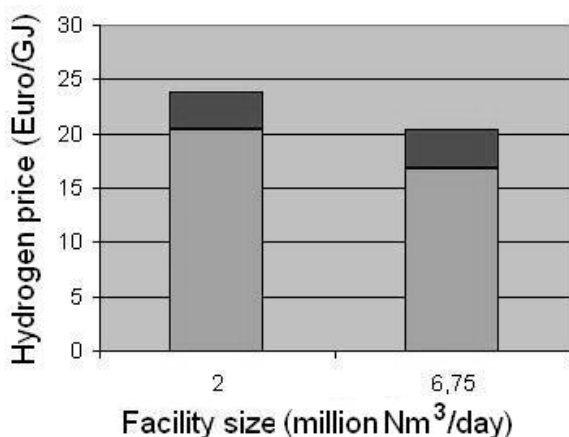


and electric power was needed to be accomplished. This technique is used for hydrogen production in small quantities on industry. Typical commercial operation pressures are 0,2 to 0,5 MPa ( $\approx 2 - 5$  atm). This operation has thermal efficiency (with hydrogen LHV) about 65% up to 75% for large units and about 50% up to 60% for small units.

Electrolysis has been considered as a "green" technique for hydrogen production, especially when electric power comes from renewable sources such

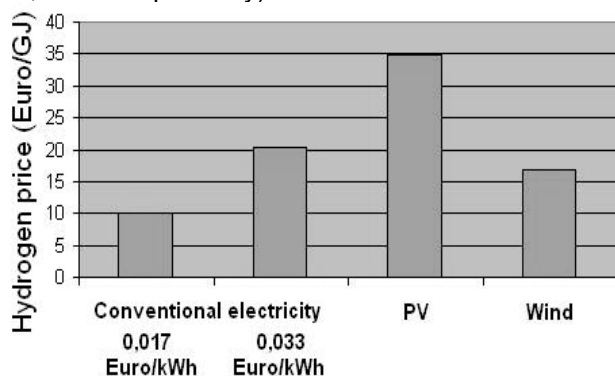
as sun, wind and biomass. On all other cases, the environmental impact is confined to the one of electric energy production.

The cost of hydrogen production from this technique is very high, especially for small units and it becomes acceptable only for units with capacity higher than 1MW. So, hydrogen sell price from this method is about 10,8€ up to 26,6 €/GJ. The major cost of production is electric power used (e.g. at 0,04€/kWh the electric power is 80% of selling price of hydrogen).



**Figure 4.** Cost of hydrogen as function of facility size for electrolysis of water

It could be possible to produce H<sub>2</sub> using photovoltaic elements or wind as a source for electric power but this has could be rather costly (about 34,8€/GJ and 16,8€/GJ respectively).



**Figure 5.** Cost of H<sub>2</sub> producing via electrolysis of water and by using different energy sources

## TECHNOLOGIES OF TOMORROW

It is obvious that the target of developed countries is the replacement of at least partly fossil fuels with renewable sources of energy, in the next two decades. As long as the environmental problems will be increasing and as Kyoto protocol countries ... to reduce carbon dioxide emissions, hydrogen production techniques from fuels free of CO<sub>2</sub> will be preferred.

In this section possible future technologies will be introduced based on their environmental benefits, advanced technology, and their capability to be adapted on today's system.

## CO<sub>2</sub> sequestration

The CO<sub>2</sub> sequestration is a today's technique available only for steam reforming. In the future main goal of scientists all over the world will be to apply this technique on the partial oxidation reaction. With CO<sub>2</sub> sequestration all classics technologies using for producing hydrogen could be applied in the future without environmental problems. The sequestrate CO<sub>2</sub> could be stored underground in old mines of NG or petroleum, or in deep ocean. Another scenario for economic management of CO<sub>2</sub> is the carbon dioxide disposal into a greenhouse assisting plant growth. Different studies have shown that the cost of sequestration raises the hydrogen sell price about 25% up to 50% and it could be applied only for steam reforming and for CO<sub>2</sub> disposal in small distances. Most probably the cost will be about the same for the partial oxidation reaction, too.

## Advanced Electrolysis

The electrolysis process is expected to be improved in the future with higher capacities on hydrogen production and lower costs. The technological improvement will be primarily on the membrane and construction materials will be following. New membranes will operate in higher temperatures and pressures, with obviously advantages the efficiency of electrolysis. Advanced materials will support higher pressures in the output of the reactor. With advanced electrolysis we could take the same quantity of hydrogen with less electric energy and in higher pressures, as the power that reaction needs, comes from the heat and the pressure of water. One very promising technology is photovoltaic system with high performance and low cost. Photovoltaic plates are constructed today as high technology systems which may have very high operating cost. On the next decade the manufacture cost of PV is expected to be decreased and furthermore the cost of hydrogen will be significantly decreased. The development of small systems that will be used as self operate stations using light and heat of the sun, will be the .... Another project could be production of hydrogen from water electrolysis using the heat and the electricity of nuclear stations. The main problem on this project is the disposal of radioactive wastes. Moreover, it was expected that in the next decades these wastes will be recycled or deactivated.

## SMR with external heat

This technique is similar, on theory, with advanced electrolysis using nuclear heat. The required heat for the SMR process we be taken from a nuclear reactor or from the steam of the power plant. The first approach could be considered as 'green' if there will

be no nuclear wastes. On the second one there will be a major problem that this technique uses fossil fuels for heat generation. So it could be used only nowadays for thermal efficiency improving in electric generation plants.

### Biomass

Biomass could be used as fuel for hydrogen production and available methods are

- Steam gasification
- Pyrolysis
- Biological hydration

#### Steam gasification

Biomass reacts with the air (oxygen) and with steam producing mixture of hydrogen and carbon monoxide called syngas. Depending on the feedstock these processes are called biomass gasification referring to solids and biomass reforming referring to gases

#### Pyrolysis

The process of pyrolysis for hydrogen production ... the decomposition of biomass at high temperatures into hydrogen and carbon. Produced carbon could be stored, achieving CO<sub>2</sub> emissions decrease in the atmosphere.

#### Biological hydration

There are many biological processes for producing hydrogen. All these method are on the first stage (research) and it is expected that in the next years some commercial systems will be installed .

### Proposed System for Hydrogen Production

Thiw system seems to fulfill all demands of tomorrow and today by using biomass as primary fuel for producing biogas which will be used as fuel for the steam reforming reaction (SMR) to be accomplished.

#### Process

Biomass is introduced into an anaerobic digester and it stays there for about 30 days, so that bacteria is growing up producing CO<sub>2</sub> and CH<sub>4</sub> at the end of their metabolism. Produced biogas could be used on SMR units to produce hydrogen or it could burned in a steam electric generator producing electric power and steam. Part of electricity and steam produced could be introduced into an advanced electrolysis unit for producing pure hydrogen. A great advantage of this project is that the plat doesn't need any external power, as it can use biogas for any energy requirement. The whole process is presented in Diagrams 1 and 2.

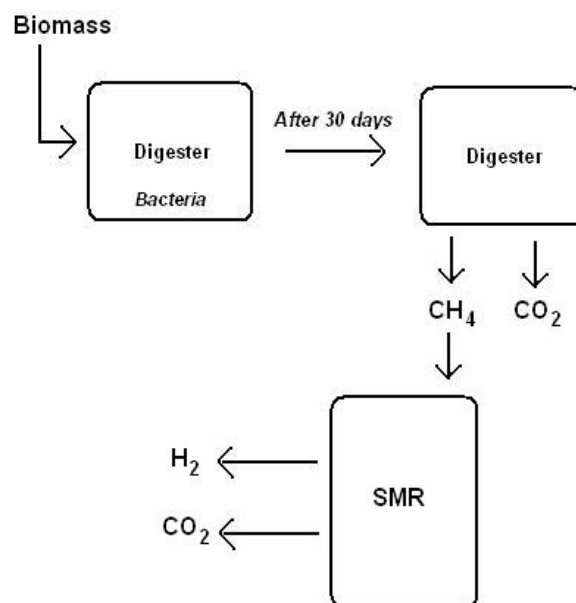


Diagram 1. Diagram of digestion and SMR unit

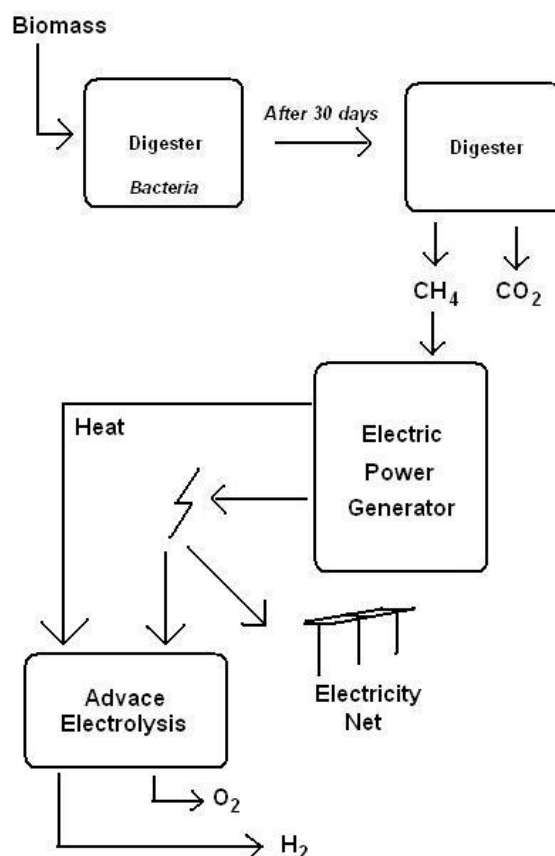


Diagram 2. Diagram of digestion, electric generation and electrolysis unit.

### Biomass origin

The biomass needed for this process could be generated from municipal or agricultural wastes or it could be produced from a food factory. Almost any organic compound could be used for producing biogas. It could be also very easy for the biological aerobic systems of a big town to be modified in anaerobic digester with obvious advantages. In the next table the mean gas yields produced from different types of agricultural biomass are presented (Table 1)

**Table 1** Mean gas yields from various types of agricultural biomass

Substrate	Gas-yield range (l/kg VS)	Average gas yield (l/kg VS)
Pig manure	340-550	450
Cow manure	150-350	250
Poultry manure	310-620	460
Horse manure	200-350	250
Sheep manure	100-310	200
Stable manure	175-320	225
Grain skew	180-320	250
Corn straw	350-480	410
Rice straw	170-280	220
Grass	280-550	410
Elephant grass	330-560	445
Bagasse	140-190	160
Vegetable residue	300-400	350
Water hyacinth	300-350	325
Algae	380-550	460
Sewage sludge	310-640	450

### Environmental impact

The process has no impact in the environment as the produced CO<sub>2</sub> came from the atmosphere with a closed carbon circle. Furthermore when biomass comes from crop CO<sub>2</sub> could be used as nutrition of the plants helping their growth.

### Cost

This project can be subsidized by European Union for the construction so the capital cost is limited. Also the crop of plants for energy production could be subsidized even though this will have no straight affect on biogas cost. On the other hand waste biomass could be used so that the cost of produced biogas will be almost zero (not energy needed for the plant).

For a significant production of hydrogen quantities the plant must be quite large. So the size of digester must be about 20000 cubic meters for a 10000 Nm<sup>3</sup> biogas per day (about 1MW electricity per hour for 17 hours a day). This system will be competitive for the fossil fuels. Industries of hydrogen doesn't need to modify their system as they can be used their existing steam reforming units. Methane concentrations produced by using different feed-stocks are presented in Table 2.

**Table 2** Methane containing in biogas producing from different feedstocks

Cattle manure	65%
Poultry manure	60%
Pig manure	67%
Farmyard manure	55%
Straw	59%
Grass	70%
Leaves	58%
Kitchen waste	50%
Algae	63%
Water hyacinths	52%

The size, the type and the material of the digester could change the capital cost. The most frequently used materials for the digester construction are:

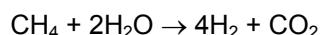
- cement
- steel and
- plastic fabric

Steel is used for medium size digester because it is very easy on construction, while on bigger plants cement is usually used. Plastic fabric often is used as a reservoir for small size biological cleaning systems. This method is very economical and it could be also used on bigger size digesters. The cost for this type of digester is about 112.000 euro. This is analyzed in the table that follows (Table3)

**Table 3.** Cost of a large size digester

Cost Analysis	Euro
Earthwork	84.000
Plastic Fabric	10.300
Plastic Fabric (cover)	14.000
Workers	4.500
<b>Total</b>	<b>112.800</b>

For evaluating the cost of hydrogen produced the following analysis could be adopted. According to the steam reforming reaction (SMR)



it could be accepted that one mole of methane produces four mole of hydrogen and the the same could be applied on gaseous phase so that from 22,4 liters of methane 89,6 liters of hydrogen will be produced. From 10000 cubic meters biogas the plat consumes about 35% so the remaining biogas is about 6500 cubic meters. Methane content in 6500 m<sup>3</sup> biogas are 4225 m<sup>3</sup> and as this quantity of methane can produce 16900 Nm<sup>3</sup> H<sub>2</sub> its selling price will be about 14€/GJ.

### Conclusions

There are many commercial technologies for hydrogen production in now days. With the environmental demands growing up and the Kyoto protocol to enforce this, a future where hydrogen will be the main fuel is coming.

Today's systems can not respond to increasing environmental demands, so there is a need for new technologies to be developed and commercialized.

Biomass is a nature fuel and with suitable processes could be used in today's system. Big industries looking for alternative fuels which can be used on today's systems, so biomass is a very promising opportunity.

System like the intended is used today for the electricity production in big farms. In the future these farms maybe become a hydrogen station, and same systems could be applied in any house for locally production.

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