



SPECIALIZATION FINAL PROJECT

Steam Reforming of Renewable Feedstock's for the  
Production of Hydrogen



Specialization Course on  
**Hydrogen Technologies and Fuel Cells**

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# Steam Reforming of Renewable Feedstock's for the Production of Hydrogen

Santos Ishikura, Caio Fabio Maciel

**Abstract:** In view of the continuing importance of the biofuels as a source of hydrogen, there is a need for a comprehensive review on this topic. The importance of process engineering related aspects is evident and these need to be discussed at length. This work is aimed at fulfilling this need. It reviews the available literature on catalytic steam reforming of biofuels. The key research issue for this concept is to demonstrate that bio-fuels can be efficiently steam reformed. All published information on this topic is analyzed and presented in a coherent manner. The role of the catalyst composition and the process conditions in determining product distribution is elucidated. The possible reaction pathways and thermodynamic considerations have also been discussed. The strategy can be applied to bio-oils, residual fractions derived from industrial operations and from ethanol production. Effluents from other biomass processing technologies such as transesterification of vegetable oils can also be attractive feedstocks for the production of hydrogen. The focus is on catalytic steam reforming of different biomass-derived liquids. It is expected that this will provide an insight into the possibilities of steam reforming of biofuels to produce hydrogen.

**Keywords:** Hydrogen, Biofuels, Steam Reforming, Renewable Feedstock.

## 1. INTRODUCCIÓN

Considerable attention was focused on the development of alternate energy sources after the energy crisis in the 1970s. The worldwide energy need has been increasing exponentially, the reserves of fossil fuels have been decreasing, and the combustion of fossil fuels has serious negative effects on environment because of carbon dioxide (CO<sub>2</sub>) emission.

Biomass is one of the few resources that have the potential to meet the challenges of sustainable and green energy systems. In order to produce useful chemicals and fuels from biomass, a system similar to a petroleum refinery is proposed, which is known as a "biorefinery". To achieve the goals of sustainable development, biorefineries have to play a dominant role in the future.

Hydrogen (H<sub>2</sub>) is nowadays considered as an alternative fuel and its use is gaining more and more acceptance as the environmental impact of hydrocarbons becomes more evident. Its production is a subject of current interest for fuel cell (FC) applications as in automotive applications or

electricity production. Fuel cells are considered to have the potential to provide a clean energy source for automotive applications as an alternative to gasoline or diesel engines. Hydrogen is also an important material in chemical synthesis and refinery for clean fuel production.

Hydrogen production is accomplished by steam reforming of natural gas and other fossil primary energy at approximately 97% of total. The possibility to obtain hydrogen, defined in all sort of scientific and technological events and reports as the future energy vector, from renewable feedstock has been reported in the bibliography.

## 2. HYDROGEN

Hydrogen is the lightest element. Although only found in the free state in trace amounts, it is the most abundant element in the universe and is present in a combined form with other elements. Water, natural gas, crude oils, hydrocarbons, and other organic fossil materials are major sources of hydrogen.

Besides H<sub>2</sub> has a high energy yield of 122 kJ/g, which is 2.75 times greater than an average hydrocarbon fuel. The major problem in utilization of hydrogen gas as a fuel is its inavailability in nature and the need for inexpensive production methods.

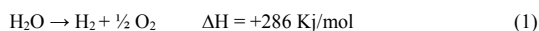
## 3. TECHNOLOGIES OF HYDROGEN PRODUCTION

Despite its abundance in the universe, H<sub>2</sub> does not occur freely on earth, as it reacts very readily with other elements. To obtain it means to remove it from these other molecules. With respect to the energy required, it is easy to remove hydrogen from compounds that are at a higher energy state, such as fossil fuels. This process releases energy, reducing the amount of process energy required. It takes more energy to extract hydrogen from compounds that are at a lower energy state, such as water, as energy has to be added to the process.

A number of hydrogen generation routes have been explored. Methanol, ethanol, ammonia, gasoline and natural gas are some possible sources of hydrogen production. In addition, petroleum distillates, liquid propane, oil, gasified coal and even gas from landfills and wastewater treatment plants can also be processed to supply hydrogen.

### 3.1. Electrolysis

In this process, electricity is used to decompose water into its elemental components: hydrogen and oxygen. To decompose water, an energy input equal to an enthalpy change of 286 KJ/mol is required:



It has high product purity and is feasible on small and large scales. At the heart of electrolysis is an electrolyzer. An electrolyzer is a series of cells each with a positive and negative electrode. The electrodes are immersed in water that has been made electrically conductive. It requires the input of large amounts of electrical energy.

In principal, electrolysis can be entirely nonpolluting and renewable. To be truly clean, the electrical power stored during electrolysis must derive from non-polluting, renewable sources. Consequently, the total environmental impact of acquiring hydrogen through electrolysis is largely dependent on the impacts of the source power.

### 3.2. Thermal Decomposition

Direct decarbonization strategy involves thermal decomposition of methane and other hydrocarbons in air and/or water-free environment in a high-temperature chemical reactor with production of hydrogen and elemental carbon



The required temperature level mentioned before, necessary to drive the process, can be supply for a renewable source. The main advantage of this approach is that the fuel has zero CO<sub>2</sub> emission: carbon as opposed to CO<sub>2</sub> is sequestered and marketable carbon black (CB) is synthesized. From the economical point of view is the production of two valuable products, hydrogen (H<sub>2</sub>) and a high-value nanomaterial, carbon black. Moreover, fossil fuels are saved with respect to the production of H<sub>2</sub> and CB by conventional methods.

### 3.3. Solar Energies Cycles

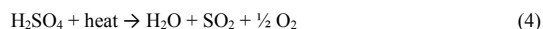
Solar energy cycles are alternative technologies for solar energy utilization. Using trough, dish, or tower concentrators, solar energy can be collected and concentrated to high energy flux and high temperature above 2000 K. The thermal energy can be used to activate chemical reactions with feedstocks, such as water, hydrogen sulfide (H<sub>2</sub>S), biomass, and fossil fuels, to produce hydrogen. Solar thermochemical cycles suitable for renewable hydrogen production include water thermolysis, H<sub>2</sub>S thermal decomposition and thermochemical water-splitting.

### 3.4. Hydrogen Production from Nuclear Power Energy

Nuclear power has been proposed for use in H<sub>2</sub> production in a few different ways. First, like any electricity-generation source to electrolysis of water, using heat from nuclear power plants to produce the steam for steam reforming or to thermally dissociate water molecules into hydrogen and oxygen.

H<sub>2</sub> can also be produced from nuclear energy through thermo-chemical processes that use high-temperature heat to dissociate water molecules. In this type of system, water is combined with sulfur dioxide (SO<sub>2</sub>) and iodine (I<sub>2</sub>) to produce sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and hydrogen iodide (HI). The H<sub>2</sub>SO<sub>4</sub> is decomposed into water, SO<sub>2</sub>, and oxygen by adding heat from the nuclear reactor at 800°C to 1000°C, and the HI is converted to H<sub>2</sub> and I<sub>2</sub>.

#### Iodine Sulfur Process Reactions



#### Overall Reaction



### 3.5. Gasification

In the gasification process, H<sub>2</sub> can be produced from a range of hydrocarbon fuels, including coal, heavy residual oils, and other low-value refinery products. The hydrocarbon fuel is reacted with oxygen in a less than stoichiometric ratio, yielding a mixture of carbon monoxide and hydrogen at 1200° to 1350°C. While these systems are less mature than steam reforming (SR), they are also relatively well established. There are various types of coal gasification systems available at present, with primary differences being the gasifier type (moving-bed, fluidized-bed, or entrained-bed), the product gas temperature, and the composition of the product gas. All of these gasifier types use steam and air or oxygen to partially oxidize coal into a gas product, and make use of the exothermic gasification reactions to produce process heat.

### 3.6. Biological Hydrogen Production

Biological hydrogen production is presently in the early development stage of laboratory-scale testing. The production processes can be divided into:

- Direct and indirect biophotolysis
- Biological water–gas shift reaction
- Photo-fermentation
- Dark fermentation

The processes are controlled by hydrogen-producing enzymes, namely, reversible hydrogenase and nitrogenase. In direct biophotolysis, microalgae absorb light energy and generate electrons. The

electrons are then transferred to Ferredoxin (FD) using the solar energy absorbed by photosystem. Then, hydrogenase can accept electrons from FD to produce hydrogen. However, direct biophotolysis is sensitive to oxygen and thus difficult to sustain hydrogen production. The indirect biophotolysis can overcome the problem by producing hydrogen and oxygen at different stages to resolve the issue of oxygen sensitivity.

In biological water gas shift reaction, some photoheterotrophic bacteria can survive in the dark by using CO as the sole carbon source to generate Adenosine Triphosphate (ATP) coupling the oxidation of CO with the reduction of H<sup>+</sup> to H<sub>2</sub>.

In photo-fermentation, photosynthetic bacteria produce hydrogen through the activity of their nitrogenase using solar energy and organic acid or biomass. Alternatively, in dark fermentation, anaerobic bacteria and some microalgae, such as green algae on carbohydrate-rich substrates, can produce hydrogen in a dark environment. Since solar irradiation is not a requirement, dark fermentation is more versatile.

### 3.7. Reforming

Reforming is a chemical process that reacts H<sub>2</sub>-containing fuels in the presence of steam, oxygen, or both into a hydrogen-rich gas stream. When applied to solid fuels the reforming process is called steam gasification. The equipment used to produce reformat is known as a reformer or fuel processor. The specific composition of the reformat depends on the source fuel and the process used, but it always contains other compounds such as nitrogen, carbon dioxide, carbon monoxide and some of the unreacted source fuel. The reforming reactions require the input of water and heat and your efficiencies are approximately 65% and low temperature methanol reformers can achieve 70 to 75%.

## 4. POTENCIAL REFORMING FUELS

In theory, any hydrocarbon or alcohol fuel can serve as a feedstock for the reforming process. Some particularly characteristics may difficult the process such as size of molecule, the main constituents of the fuel, impurities (such as sulfur), as well as undesirable compounds (namely olefins and aromatics). Naturally, fuels with existing distribution infrastructures are the most commonly used.

Methanol, which is mainly prepared by synthesis gas conversion, has a favorable H:C ratio of 4, is largely distributed and is available in abundance. Moreover, it can be transported and reformed more easily than natural gas. However, its main drawback is its high toxicity. Ethanol is more promising since it is less toxic. It can also be more easily stored and safely handled. Glycerol can be regarded as an example of such a feedstock because it is formed in large

quantities as the byproduct of the biodiesel production and in the saponification of triglycerides in the production of free fatty acids for detergents

Utilization of wide variety of gaseous, liquid and solid carbonaceous wastes was also investigated as renewable sources.

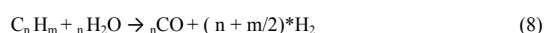
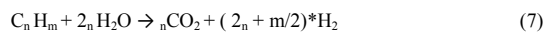
Biomass can be used as renewable resources for hydrogen gas production. Conversion of biomass to hydrogen is potentially an economically viable opportunity utilizing domestically available resources. The most commonly used techniques for biomass reforming are gasification and pyrolysis.. Alternatively, hydrogen can be directly obtained from aqueous-phase reforming (APR) of glucose without formation of char. The APR reactions of glucose were only successful at very low concentrations of glucose (1%), whereas high biomass concentration will be necessary to reach commercial goals.

## 5. GENERAL PRINCIPLES OF STEAM REFORMING

Most hydrogen production occurs by SR; is the oldest and most widely used technology: converting a hydrocarbon–steam mixture into a mixture of (primarily) H<sub>2</sub> and CO<sub>2</sub>. Steam reforming is achieved by reaction over a catalyst at high temperature. In addition to the energy required to provide the steam, the overall reaction is endothermic.

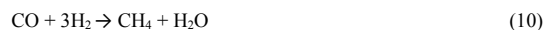
The first step of the process is the reforming. This reaction is carried out in the range of temperatures 673–1273 K. Reforming can be either by steam (steam reforming), or by humidified air (partial oxidation reforming), or by a mixture of air and steam (auto-thermal reforming). Compared with partial oxidation and autothermal reforming, catalytic steam reforming offers higher hydrogen concentrations.

The stoichiometry of hydrocarbon reforming for maximum hydrogen production is described by the follows equations:



The initial steps in steam reforming are dissociative adsorption of the hydrocarbons on the metal sites of the catalyst and reaction of the adsorbed C<sub>x</sub>H<sub>v</sub> species with adsorbed H<sub>2</sub>O-derived species to produce CO and H<sub>2</sub> (Eq. (8)). With an active catalyst at temperatures below 600°C, reforming of naphtha (Eq. (8)) is irreversible, with no intermediates, and the only byproduct is carbon that forms on the catalyst. The reversible reactions are the water-gas shift (WGS) reaction (Eq. (9)), the methanation

reaction (Eq. (10)), and the disproportionation of CO (Eq. (12)), which are equilibrium limited.



The reformed fuel often contains other gases such as CO. Except for use in high temperature fuels cells (HTFC), the CO concentration must be reduced to a very low level (around 10 ppm). Various options for CO reduction include water–gas shift (WGS), preferential oxidation of CO, methanation, membrane separators and combinations of these with the reforming reactor. In essence, reforming a fuel consists of the following steps:

- Feedstock purification (including sulfur removal).
- Steam reforming of feedstock to form hydrogen and carbon oxides.
- Primary purification—conversion of carbon monoxide to carbon dioxide.
- Secondary purification—further reduction of carbon monoxide.

Normally, a WGS process is chosen as primary purification. In the WGS, carbon monoxide is reacted with steam to give CO<sub>2</sub> and H<sub>2</sub>. The reaction is exothermic and independent of pressure. Commonly It consist in a two steps process, high temperature and low temperature water gas shift (HTS and LTS), that increase the H<sub>2</sub>:CO ratio and, consequently, reduce the CO content of this gas stream. The residual CO can be then reduced further to ppm level in a CO preferential oxidation (PROX) reactor as a second purification. In order to maximize the hydrogen yield, an excess of water is usually fed to carry out the water gas shift reaction. Exit gases from the shift conversion are treated to remove carbon dioxide. This may be done by absorbing carbon dioxide in a physical or chemical absorption solvent or by adsorbing it using a special type of molecular sieves. Carbon dioxide, recovered from the treatment agent as a byproduct, is mainly used with ammonia to produce urea.

The important process variables are reactor temperature, residence time, catalyst and steam/carbon ratio. Feed characteristics are also considered, since they influence the process severity.

### 5.1. Steam Reforming of Hydrocarbon

The most economical way to produce hydrogen is by steam reforming of petroleum fractions and natural gas. The reaction is a catalytic process that typically takes place in vapour phase at atmospheric pressure and temperatures around 1073 K. Catalysts for steam reforming of hydrocarbons are mainly based on nickel as active component supported on oxides

with high thermal stability. The feed to the shift converter contains large amounts of carbon monoxide which should be oxidized. An iron catalyst promoted with chromium oxide is used at a temperature range of 425–500°C to enhance the oxidation. The product is a pure hydrogen gas containing small amounts of carbon monoxide and carbon dioxide.

The main advantage of reforming fossil fuels is that it is a mature technology that uses existing fuel infrastructures. It reduces the need to transport and store hydrogen. It is the less expensive process than other hydrogen production methods.

The disadvantages are usually associated with the reformers. They are complex, large and expensive, can have relatively long warm-up times and can introduce additional losses into the energy conversion process. In terms of contamination, the pollution generated by reformers take three forms: CO<sub>2</sub> emissions, incomplete reactions, leaving CO and some of the source fuel in the reformat and production of pollutants through combustion, such as nitrous oxides.

The design of the steam reforming process of CH<sub>4</sub> is explained referring to figure 1:

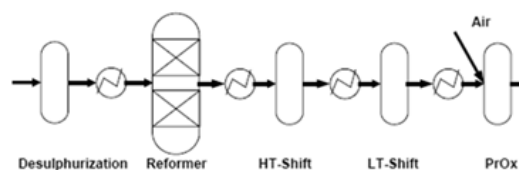


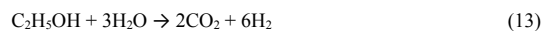
Figure 1: Principles scheme of a steam reforming process.

### 5.2. Steam Reforming of Ethanol

Ethanol is easier and safer to store and transport due to its low toxicity and volatility, and for being biodegradable. Ethanol presents several advantages related to natural availability, storage and handling safety. It can be produced renewably from several biomass sources, including energy plants, waste materials from agro industries or forestry residue materials, organic fraction of municipal solid waste, etc.

In addition, the bio ethanol-to-hydrogen system has the significant advantage of being nearly CO<sub>2</sub> neutral, since the carbon dioxide produced is consumed for biomass growth, thus offering a nearly closed carbon loop while the use of methanol and gasoline adds to CO<sub>2</sub> emissions.

The first step in the conversion of ethanol to hydrogen is reforming. The bioethanol steam reforming is an endothermic reaction carried out in the range of temperatures 673–1273 K, for this reason the necessary heat has to be supplied from an external source; it could be represented in the simplest case by the following stoichiometry equation:



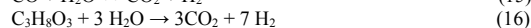
Both reactants (water and ethanol) includes hydrogen atoms that contribute to the total yield and the thermal efficiency obtained is considerably good (>85%)

Ethanol is first dehydrogenated to acetaldehyde which subsequently decomposes to CH<sub>4</sub> and CO. These lead to the formation of H<sub>2</sub> and CO<sub>2</sub> by steam reforming and water gas shift (WGS) reactions. Thus, the exit stream composition is governed by CH<sub>4</sub> steam reforming and WGS reactions. Ethanol has relatively high hydrogen content; the key aim of this process is to maximize H<sub>2</sub> production, discouraging at the same time side reactions as ethanol dehydration and decomposition that lead to produce undesirable products, such as methane, diethyl ether or acetic acid that compete for hydrogen atoms, which causing the reduction of the global yield.

### 5.3. Steam Reforming of Glycerol

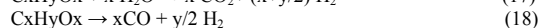
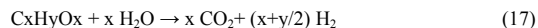
Glycerol can be efficiently converted in hydrogen by means of its catalytic reaction with steam. In the steam reforming of glycerin, synthesis gas that contains both carbon monoxide (CO) and hydrogen (H<sub>2</sub>) is produced. From syngas, methanol, which is used for methyl esterification of vegetable oils, can be produced using conventional technology and, as a result, 100% biomass-based bio-diesel fuel could be produced.

The process involves complex reactions. As a result, several intermediate byproducts are formed and end up in the product stream affecting final purity of the H<sub>2</sub> produced. Furthermore, the yield of the hydrogen depends on several process variables, such as system pressure, temperature, and water-to-glycerol feed ratio (WGFR). The overall reaction of hydrogen production by steam reforming of glycerol is:



The steam reforming of glycerol produces H<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>, and C, together with the unreacted water and glycerol. Only these compounds are the primary products formed in the reaction. CH<sub>4</sub> competes against H<sub>2</sub>, and obviously CH<sub>4</sub> is not a desirable product. Since the decomposition of glycerol to CH<sub>4</sub> is highly favorable during the reforming process, the catalyst must have sufficient capacity for reforming the produced CH<sub>4</sub> into hydrogen and carbon monoxide. Carbon will cause deactivation of the catalyst.

According to reaction 17, complete steam reforming of glycerol could provide a gas with a maximum hydrogen content of 70%, while reaction 18 suggests glycerol decomposition could lead to a hydrogen content of 57%.



The feasibility of hydrogen production from glycerol steam reforming show that the upper limit of the moles of hydrogen produced per mole of glycerol is 6 at 960 K, WGFR=9:1, and P =1 atm vs the stoichiometric value of 7.

## 6. CONCLUSIONS

The global and equilibrium analyses, both show a decrease in thermal efficiency for reforming larger hydrocarbons compared to methane. H<sub>2</sub> and electricity seem to be the key solutions for the 21st century, enabling clean efficient production of power and heat from a range of primary energy sources. Today, hydrogen is mainly produced from natural gas via steam methane reforming, a process suffering from several limitations, like the thermodynamic equilibrium limitations, high energy demand, catalyst deactivation due to carbon deposition and increased CO<sub>2</sub> emissions.

From the process engineering point of view, the following issues need to be addressed: reforming should preferably be carried out at low temperatures and atmospheric pressures to reduce the operating costs; the catalyst should provide high selectivity to H<sub>2</sub> and inhibit CO and by-products formation such as methane; the catalyst must resist coke formation which reduces the number of active sites and hence the reaction rates and implies regeneration process which are costly.

Feedstock issues, such as supply, cost, logistics and the value of coproducts, are major factors in cost-effectiveness of the hydrogen production process. Work is in progress to develop decision models for selecting among feedstock, process, and deployment alternatives.

Moreover, a reexamination of the road transportation throughout the world is being pursued on the grounds of (i) the increasing concern about the environmental consequences of fossil fuels used for vehicles propulsion; (ii) the global earth warming; (iii) the growing dependence of the industrialized countries on fossil oils; and (iv) the increasing global awareness of how human activities influence the environment and how a sustainable development can be achieved with the increasing world population. This brought about always further and further restrictive emission legislations all over the world, in line with the Kyoto Protocol, which paves the way to the introduction of zero-emission vehicles (ZEVs). This results in ever-increasing attention on the hydrogen utilization as energy vector.

## 7. ACKNOWLEDGEMENTS

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## **Abstract**

In view of the continuing importance of the biofuels as a source of hydrogen, there is a need for a comprehensive review on this topic. The importance of process engineering related aspects is evident and these need to be discussed at length. This work is aimed at fulfilling this need. It reviews the available literature on catalytic steam reforming of biofuels. The key research issue for this concept is to demonstrate that bio-fuels can be efficiently steam reformed. All published information on this topic is analyzed and presented in a coherent manner. The role of the catalyst composition and the process conditions in determining product distribution is elucidated. The possible reaction pathways and thermodynamic considerations have also been discussed. The strategy can be applied to bio-oils, residual fractions derived from industrial operations and from ethanol production. Effluents from other biomass processing technologies such as transesterification of vegetable oils can also be attractive feedstocks for the production of hydrogen. The focus is on catalytic steam reforming of different biomass-derived liquids. It is expected that this will provide an insight into the possibilities of steam reforming of biofuels to produce hydrogen.



## 1. INTRODUCTION AND BACKGROUND

Considerable attention was focused on the development of alternate energy sources after the energy crisis in the 1970s [1-4]. The worldwide energy need has been increasing exponentially, the reserves of fossil fuels have been decreasing, and the combustion of fossil fuels has serious negative effects on environment because of carbon dioxide (CO<sub>2</sub>) emission.

A sustainable high quality of life cannot be kept apart from the worldwide supply of clean, safe, reliable, and secure energy. The European “World Energy Technology and Climate Policy Outlook” (WETO) predicts, for primary energy, an average growth rate worldwide of 1.8% per year for the period 2000-2030 [5]. The increased demand will be largely satisfied by fossil fuel reserves that, however, (i) emit either greenhouse gases or other pollutants, (ii) are not unlimited, and (iii) will then become increasingly expensive [6].

Biomass is one of the few resources that have the potential to meet the challenges of sustainable and green energy systems. In order to produce useful chemicals and fuels from biomass, a system similar to a petroleum refinery is proposed, which is known as a “biorefinery”, and the details regarding biorefineries can be found elsewhere. According to the National Renewable Energy Laboratory (NREL), “a biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass” [7]. To achieve the goals of sustainable development, biorefineries have to play a dominant role in the future. The main goal of a biorefinery is to produce high-value low-volume chemicals and low-value high-volume fuels with a series of unit operations.

Hydrogen (H<sub>2</sub>) is nowadays considered as an alternative fuel and its use is gaining more and more acceptance as the environmental impact of hydrocarbons becomes more evident. Its production is a subject of current interest for fuel cell (FC) applications as in automotive applications or electricity production. Fuel cells are considered to have the potential to provide a clean energy source for automotive applications as an alternative to gasoline or diesel engines. Hydrogen is also an important material in chemical synthesis and refinery for clean fuel production.

Hydrogen production is accomplished by steam reforming of natural gas and other fossil primary energy at approximately 97% of total [8]. The possibility to obtain hydrogen, defined in all sort of scientific and technological events and reports as the future energy vector, from renewable feedstock has been reported in the bibliography of this paper.



## 2. GOALS OF THE STUDY

The present project is carried out as final thesis in the Specialization on Hydrogen Technologies and Fuel Cells course of the University of Zaragoza, Spain through the Centro de Investigación de Recursos y Consumos Energéticos (CIRCE) of the academic year of 2007.

The objective of the study is to clarify the possibility to establish a process for the handling different biomass-derived liquids, transforming it in a high value product, hydrogen. It reviews the available literature on catalytic steam reforming of biofuels demonstrating the efficiency of the process. The study should clarify the technical aspects, as well as the environmental impacts.



### 3. HYDROGEN

Nowadays, there is an increasing interest in hydrogen as an energy carrier because it creates almost no pollution (your pollution character is related with the production method applied that will be discuss later). It is a clean fuel with no CO<sub>2</sub> emissions. Its combustion does not result in any emission other than water vapor (although under certain air/hydrogen ratios, oxides of nitrogen (NO<sub>x</sub>) can also be produced) and hence it is the least polluting fuel that could be used in an internal combustion engine.

Hydrogen is the lightest element. Although only found in the free state in trace amounts, it is the most abundant element in the universe and is present in a combined form with other elements. Water, natural gas, crude oils, hydrocarbons, and other organic fossil materials are major sources of hydrogen.

Besides H<sub>2</sub> has a high energy yield of 122 kJ/g, which is 2.75 times greater than an average hydrocarbon fuel. The major problem in utilization of hydrogen gas as a fuel is its inavailability in nature and the need for inexpensive production methods. It can be used in combustion devices or fuel cells without any carbon emissions, and minimal emissions of other pollutant gases. FC transforms chemical energy directly into electrical energy. Its theoretical efficiency, unlike conventional power generation plants or internal combustion engine, is not limited by the Carnot inefficiency problems [9]. It can be stored and transported, much like other gaseous fuels, though an infrastructure will have to be developed.

Hydrogen is the future fuel, basically since its combustion only produces water. Nevertheless, some considerations must be made about this asseveration. Firstly, if the combustion of hydrogen is performed with air at high temperatures, nitrogen oxides will also be produced. Second, as mentioned before, hydrogen is not free in Nature; this element is present in hydrocarbons and in the water. Energy has to be consumed in order to separate it from carbon (hydrocarbons) or from oxygen (water). Only if this energy is produced from renewable sources such as solar or wind energy, it can be said that hydrogen is obtained using a non-pollutant process.

#### 3.1. Technologies of Hydrogen Production

The fundamental question underlying the use of hydrogen is, where do we get it from? Despite its abundance in the universe, H<sub>2</sub> does not occur freely on earth, as it reacts very readily with other elements. For this reason, the vast majority of hydrogen is bound into molecular compounds. To obtain hydrogen means to remove



it from these other molecules. With respect to the energy required, it is easy to remove hydrogen from compounds that are at a higher energy state, such as fossil fuels. This process releases energy, reducing the amount of process energy required. It takes more energy to extract hydrogen from compounds that are at a lower energy state, such as water, as energy has to be added to the process.

A number of hydrogen generation routes have been explored. Methanol, ethanol, ammonia, gasoline and natural gas are some possible sources of hydrogen production. In addition, petroleum distillates, liquid propane, oil, gasified coal and even gas from landfills and wastewater treatment plants can also be processed to supply hydrogen. For stationary applications, natural gas is the fuel of choice due to its availability and ease in distribution. For automotive applications, gasoline is the most convenient fuel since it can be easily transported. However, some FC are very sensitive to impurities in fuel and have a sulphur specification less than 1 ppm. Ammonia is toxic and poses a problem of generating nitrogen oxides during catalytic combustion of the cell effluent [10].

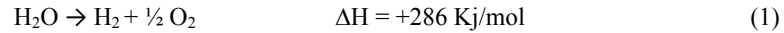
Hydrogen is produced commercially on a large scale mainly by steam reforming, partial oxidation, coal gasification and electrolysis. Alternative methods of hydrogen production include thermochemical water decomposition, photoconversions, photobiological processes, production from biomass, and industrial processes. Although some of these methods show promise for the future, they are still largely experimental and capable of supplying only small amounts of hydrogen.

Large-scale production benefits from economies of scale and plants can be located near power and water, but suffers from the difficulties of hydrogen transportation. Some methods of hydrogen production such as from coal or biomass, can only be undertaken on a large scale. H<sub>2</sub> can be produced in small scale as well. This scale production can reduce the problems of hydrogen transportation by using energy that is easily brought to the facility, such as electricity, natural gas or solar. On the downside, the amount of equipment required for the amount of hydrogen produced is significantly higher than for large scale facilities, due to the economy of scale. At the extreme small scale, fossil fuels could be reformed to hydrogen on board a fuel cell vehicle, but the systems are complex and costly.



### 3.1.1. Electrolysis

The process of extracting hydrogen from water is called electrolysis. In this process, electricity is used to decompose water into its elemental components: hydrogen and oxygen. To decompose water, an energy input equal to an enthalpy change of 286 KJ/mol is required:



It has high product purity and is feasible on small and large scales. At the heart of electrolysis is an electrolyzer. An electrolyzer is a series of cells each with a positive and negative electrode. The electrodes are immersed in water that has been made electrically conductive. It requires the input of large amounts of electrical energy; since the electricity costs account for 80% of the operating cost of H<sub>2</sub> production, electrolysis should be used in areas where electricity is inexpensive. In addition, feed water has to be demineralized to avoid deposits on the electrodes and corrosion [11].

Electrolysis is often touted as the preferred method of H<sub>2</sub> production as it is the only process that does not need relying on fossil fuels. In principal, electrolysis can be entirely nonpolluting and renewable. To be truly clean, the electrical power stored during electrolysis must derive from non-polluting, renewable sources. If the power is derived from natural gas or coal, the pollution has not been eliminated, only pushed upstream. In addition, every energy transformation has an associate energy loss. Consequently, fossil fuels may be used with greater efficiency by means other than by driving the electrolysis of hydrogen. Consequently, the total environmental impact of acquiring hydrogen through electrolysis is largely dependent on the impacts of the source power.

### 3.1.2. Thermal Decomposition

Direct decarbonization strategy involves thermal decomposition (TD) (or cracking, pyrolysis) of methane and other hydrocarbons in air and/or water-free environment with production of hydrogen and elemental carbon



The process thermally decomposes methane in a high-temperature chemical reactor. Such a decomposition, which is nearly as endothermic as the



vapor reforming one (relative to the hydrogen produced) may be performed at high temperatures ( 1500-2000 K) using an energy supply [12].

There have been attempts to use different catalysts to reduce the maximum temperature of TD of methane. Metal catalysts, including Ni, Fe, Co, Pd and others, have been most commonly used for methane decomposition. However, there was a catalyst deactivation problem associated with the carbon build up on the catalyst surface [13].

In most processes, steam conversion is used. A big disadvantage of such processes is that the production of hydrogen is accompanied by the emission of large quantities of CO into the atmosphere, one part coming from the conversion and another as a result of the combustion of a part of the methane. The use of water which induces CO<sub>2</sub> production, may be avoided by using a simple thermolysis process.

Thermolysis process does not include Water gas-shift and CO<sub>2</sub> removal stages, which significantly simplifies the process. In addition to hydrogen as a major product, the process produces a very important byproduct: clean carbon. A key point of the process economics is the added value of the produced Carbon. The selling price depends on the product nano-structure and applications in the fields of polymer composites and batteries are targeted [14].

The required temperature level mentioned before, necessary to drive the process, can be supply for a renewable source. In this point of view the decarbonisation of methane or natural gas is a mid-term route for producing hydrogen in a large scale from renewable energy without greenhouse gas emission. The main advantage of this approach is that the fuel has zero CO<sub>2</sub> emission: carbon as opposed to CO<sub>2</sub> is sequestered and marketable carbon black (CB) is synthesized. The energy carrier H<sub>2</sub> is thus produced with renewable energy. From the economical point of view is the production of two valuable products, hydrogen (H<sub>2</sub>) and a high-value nanomaterial, carbon black. Moreover, fossil fuels are saved with respect to the production of H<sub>2</sub> and CB by conventional methods [15].

### 3.1.3. Solar energy cycles

Solar energy cycles are alternative technologies for solar energy utilization. Using trough, dish, or tower concentrators, solar energy can be



collected and concentrated to high energy flux and high temperature above 2000 K. The thermal energy can be used to activate chemical reactions with feedstocks, such as water, hydrogen sulfide (H<sub>2</sub>S), biomass, and fossil fuels, to produce hydrogen. Solar thermochemical cycles suitable for renewable hydrogen production include water thermolysis, H<sub>2</sub>S thermal decomposition and thermochemical water-splitting.

### 3.1.3.1. Solar water thermolysis

Solar water thermolysis is the direct dissociation of water into hydrogen and oxygen gas by using concentrated solar thermal energy at high temperature above 2000K [16]. The process is conceptually simple, but operating at such high temperature requires special material selection. The efficiency is low mainly because of re-radiation loss and energy loss in gas separation by rapid quenching. The gas separation process will also generate explosive mixtures.

### 3.1.3.2. Hydrogen sulfide

Toxic hydrogen sulfide (H<sub>2</sub>S) is a commonly found unwanted by-product in the petroleum, petrochemical, and mineral-processing industries. Conventional methods for H<sub>2</sub>S removal are absorption in caustic solution and catalytic oxidation in the Claus process, which is costly and consumes H<sub>2</sub> by oxidation to H<sub>2</sub>S to produce low-quality process heat [17]. Solar thermal decomposition of H<sub>2</sub>S offers an economical way to convert toxic H<sub>2</sub>S into useful hydrogen fuel. At 1800K and 0.33 bar, 70% H<sub>2</sub>S can be converted into H<sub>2</sub> and S [17]. At such high temperatures, hydrogen and sulphur gas can be separated by fast quenching to solidify the sulfur or by membrane separation.

### 3.1.3.3. Thermochemical Watersplitting

Hydrogen could be produced by thermochemical water-splitting, a chemical process that effects the multistep decomposition of water [18]. The process consists of both endothermic and exothermic reactions. Water and heat are the inputs, and hydrogen and oxygen are the only outputs. The other chemicals and reagents are recycled in a closed cycle.



#### Overall Reaction





The simplest thermochemical process to split water involves heating it to a high temperature and separating the hydrogen from the equilibrium mixture. Unfortunately, the decomposition of water does not proceed well until the temperature is very high.

Compared to electrochemical water-splitting cycles, thermochemical cycles have a potential advantage; efficiency losses due to heat transformation to electricity do not occur [19].

Heat can be produced by nuclear means, using an advanced high-temperature nuclear reactor as the energy source (4th generation of nuclear reactors). Another possibility is the use of the energy source from concentrated solar energy. Since hydrogen produced by thermochemical water splitting does not contain contaminants, it could be used directly in fuel cells.

As mentioned before, thermochemical water-splitting consists of the conversion of water into hydrogen and oxygen by a series of endothermic and exothermic chemical reactions. Endothermic reactions can be driven by solar thermal energy. The process would be much more environmentally acceptable.

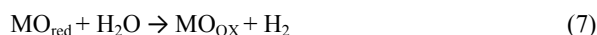
A few cycles have been studied for solar hydrogen production. The current state-of-the-art of solar chemistry for water splitting and hydrogen production is focused on the so-called redox pair cycles. These are two-step processes, based on redox materials that can act as effective water splitters at lower temperatures [20].

They are mainly the two-step cycles based on metallic oxides [21], such as ZnO/Zn, Fe<sub>3</sub>O<sub>4</sub>/FeO, and the associated cycles (involving ferrites). The generic two-step process makes use of metal oxides as a redox pair MO<sub>ox</sub>/MO<sub>red</sub> according to the following reactions:

**Activation step**



**Hydrogen generation step**





According to this idea, in the first step (water splitting) the activated redox reagent is oxidized by taking oxygen from water and producing hydrogen. During the second step the oxidized state of the reagent is reduced, to be used again (regeneration), delivering some of the oxygen of its lattice. The disadvantage is that a two-step process is required, consisting of a water splitting and a regeneration (oxygen release) step. The advantage is the production of pure hydrogen and the removal of oxygen in separate steps, avoiding the need for high-temperature separation and the chance of explosive mixtures formation.

#### **3.1.3.4. Photocatalytic and photoelectrochemical hydrogen production**

Photocatalytic and photoelectrochemical conversions are other hydrogen production methods using solar energy. When a semiconductor is irradiated by photons having energy equal to or above the band gap energy, electrons can be promoted from the valence band to the conduction band, leaving a positively charged hole in the valence band. If the conduction band edge is more negative than the hydrogen production level and the valence band edge is more positive than the oxygen production level, the photo-generated electron/hole pairs are able to decompose water into oxygen and hydrogen [17]. However, with the present development, the hydrogen production rate is still low due to the following reasons:

- Quick electron/hole recombination in the bulk or on the surface of semiconductor particles,
- Quick back reaction of oxygen and hydrogen to form water on the surface of catalyst
- Inability to utilize visible light.

Separation of hydrogen gas is required in photocatalytic hydrogen production as oxygen and hydrogen are produced simultaneously. This can be achieved by employing a photoelectrochemical system [22], in which hydrogen and oxygen are produced at different electrodes. It is expected that photocatalytic and photoelectrochemical hydrogen production will play an important role in the hydrogen economy.

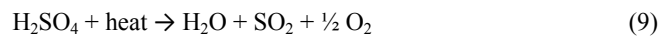
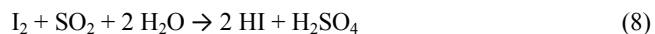


### 3.1.4. Hydrogen Production from Nuclear Power Energy

Nuclear power has been proposed for use in H<sub>2</sub> production in a few different ways. First, like any electricity-generation source, nuclear power can be used to produce H<sub>2</sub> via the electrolysis of water (H<sub>2</sub>O). Another alternative, hydrogen could be produced through steam reformation of natural gas, using heat from nuclear power plants to produce the steam. This reduces the natural gas requirements associated with operating a boiler to raise the steam, and leads to hydrogen production with less natural gas input. Other possibility, hydrogen could be produced from water by using heat from nuclear plants to thermally dissociate water molecules into hydrogen and oxygen.

Nuclear-assisted steam reforming is an option for hydrogen production, whereby the heat required for the endothermic reforming process is provided by the high-temperature heat from the nuclear reactor rather than from the combustion of natural gas. In this case, the natural gas input acts only as a source for hydrogen [23]. H<sub>2</sub> can also be produced from nuclear energy through thermo-chemical processes that use high-temperature heat to dissociate water molecules. In this type of system, water is combined with sulfur dioxide (SO<sub>2</sub>) and iodine (I<sub>2</sub>) to produce sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and hydrogen iodide (HI). The sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) is decomposed into water, SO<sub>2</sub>, and oxygen by adding heat from the nuclear reactor at 800°C to 1000°C, and the HI is converted to H<sub>2</sub> and I<sub>2</sub>. The iodine and sulfur dioxide are then re-used in the first reaction, with the oxygen being vented or potentially captured for industrial uses [23]. The following reactions are involved in this type of system:

#### Iodine Sulfur Process Reactions



#### Overall Reaction



### 3.1.5. Gasification of Coal and Other Hydrocarbons

In the partial oxidation (POx) process, also known more generally as “gasification,” hydrogen can be produced from a range of hydrocarbon fuels, including coal, heavy residual oils, and other low-value refinery products. The hydrocarbon fuel is reacted with oxygen in a less than stoichiometric ratio,



yielding a mixture of carbon monoxide and hydrogen at 1200° to 1350°C. While these systems are less mature than steam reforming (SR) for hydrogen production, they are also relatively well established. There are various types of coal gasification systems available at present, with primary differences being the gasifier type (moving-bed, fluidized-bed, or entrained-bed), the product gas temperature, and the composition of the product gas. All of these gasifier types use steam and air or oxygen to partially oxidize coal into a gas product, and make use of the exothermic gasification reactions to produce process heat. Table 1, below, shows a comparison of typical effluent streams from POx-based reformation of coal, compared with SR of natural gas.

**Table 1: Typical reformer effluent for SR of natural gas and Pox reformation of coal (percent by volume bass).**

Reformer Effluent	SMR of Natural Gas		Fluidized-Bed POx Reformation of Coal	Entrained-Bed POx Reformation of Coal <sup>a</sup>
	Reformer Effluent	Shifted Reformate		
H <sub>2</sub>	46.3	52.9	28.3	28.0
CO	7.1	0.5	33.1	47.9
CO <sub>2</sub>	6.4	13.1	15.5	6.2
CH <sub>4</sub>	2.4	2.4	4.6	0.2
N <sub>2</sub>	0.8	0.8	0.6	1.6
H <sub>2</sub> O	37.0	30.4	16.8	14.0
<b>Total</b>	<b>100.0</b>	<b>100.0</b>	<b>98.9</b>	<b>97.9</b>

Source: Hirschenhofer et al. 2000  
 Note a: Reformer effluent values shown are the average of four different entrained-bed coal reformation technologies. These emissions vary somewhat by technology.

As with all hydrogen production pathways that use fossil fuels as feedstock, but even more so with the use coal, post-processing of the effluent gas is typically required to remove compounds that are contaminants for most FC types. These include hydrogen disulfide (S<sub>2</sub>H and other sulfur compounds, ammonia, carbon monoxide (CO), and tars, oils, and phenols. The various systems needed to remove these compounds depend on the composition of the coal used, but all add cost and complexity to the production process and in many cases have specific temperature requirements that necessitate the extensive use of heat exchanger systems. Table 1 above, provides a comparison of typical natural gas reforming and coal gasification effluent compositions on a volume basis, with CO<sub>2</sub> plus CO levels on the order of double those of hydrogen in the coal systems, and with three to four times more H<sub>2</sub> than CO<sub>2</sub> plus CO produced with the natural gas systems. This suggests that for coal gasification for H<sub>2</sub> production to be practical in the long term, these CO<sub>2</sub> emissions (once the CO is converted to CO<sub>2</sub>) would need to be captured and stored.



### 3.1.6. Biological hydrogen production

Biological hydrogen production is presently in the early development stage of laboratory-scale testing. The production processes can be divided into:

- Direct and indirect biophotolysis
- Biological water–gas shift reaction
- Photo–fermentation
- Dark fermentation

The processes are controlled by hydrogen-producing enzymes, namely, reversible hydrogenase and nitrogenase [17]. In direct biophotolysis, microalgae, such as green algae and Cyanobacteria, absorb light energy and generate electrons. The electrons are then transferred to Ferredoxin (FD) using the solar energy absorbed by photosystem I. Then, hydrogenase can accept electrons from FD to produce hydrogen. However, direct biophotolysis is sensitive to oxygen and thus difficult to sustain hydrogen production. The indirect biophotolysis can overcome the problem by producing hydrogen and oxygen at different stages to resolve the issue of oxygen sensitivity [75].

In biological water gas shift reaction, some photoheterotrophic bacteria, such as *Rhodospirillum rubrum*, can survive in the dark by using CO as the sole carbon source to generate Adenosine Triphosphate (ATP) coupling the oxidation of CO with the reduction of H<sup>+</sup> to H<sub>2</sub> [17].

In photo-fermentation, photosynthetic bacteria produce hydrogen through the activity of their nitrogenase using solar energy and organic acid or biomass. The drawbacks of photo-fermentation are the high energy demand for the use of nitrogenase enzyme, low solar energy conversion efficiency, and substantial land needed for anaerobic photobioreactors. Alternatively, in dark fermentation, anaerobic bacteria and some microalgae, such as green algae on carbohydrate-rich substrates, can produce hydrogen in a dark environment. Since solar irradiation is not a requirement, dark fermentation is more versatile [75].

### 3.1.7. Reforming

Reforming is a chemical process that reacts H<sub>2</sub>-containing fuels in the presence of steam, oxygen, or both into a hydrogen-rich gas stream. When applied to solid fuels the reforming process is called steam gasification. The resulting H<sub>2</sub>-rich gas mixture is called reformat. The equipment used to produce reformat is known as a reformer or fuel processor. The specific composition of



the reformato depends on the source fuel and the process used, but it always contains other compounds such as nitrogen, carbon dioxide, carbon monoxide and some of the unreacted source fuel. When hydrogen is removed from the reformato, the remaining gas mixture is called raffinate.

The reforming reactions require the input of water and heat. Overall reformer thermal efficiency is calculated as the Low heat value (LHV) of the product hydrogen divided by the LHV of the total input fuel. This thermal efficiency depends on the efficiencies of the individual processes, the effectiveness to which heat can be transferred from one process to another, and the amount of energy that can be recovered through means such as turbochargers. In the end, high temperature reformer efficiencies are approximately 65% and low temperature methanol reformers can achieve 70 to 75%.

### 3.2. Potencial Reforming Fuels

In theory, any hydrocarbon or alcohol fuel can serve as a feedstock for the reforming process. Some particularly characteristics may difficult the process such as size of molecule, the main constituents of the fuel, impurities (such as sulfur), as well as undesirable compounds (namely olefins and aromatics). Naturally, fuels with existing distribution infrastructures are the most commonly used.

Methanol, which is mainly prepared by synthesis gas conversion, has a favorable H:C ratio of 4, is largely distributed and is available in abundance. Moreover, it can be transported and reformed more easily than natural gas. However, its main drawback is its high toxicity. Ethanol is more promising since it is less toxic. It can also be more easily stored and safely handled.

Glycerol can be regarded as an example of such a feedstock because it is formed in large quantities as the byproduct in the saponification of triglycerides in the production of free fatty acids for detergents and of fatty esters for biofuels. With the increased production of biodiesel, a glut of glycerol has been created [24] which not only has reduced world glycerol market prices but also has generated environmental concerns associated with contaminated glycerol disposal [25]. In fact, glycerol is becoming a cheap, large-volume market product, and the ability to use it as a source of organic carbon, and as a starting material for chemical transformations, is very appealing. In this context, glycerol steam reforming could



be an interesting alternative to convert the glycerol and to economically promote the transesterification process.

Utilization of wide variety of gaseous, liquid and solid carbonaceous wastes was investigated by Kim [26] as renewable sources for formation of hydrogen gas by SR.

Biomass can be used as renewable resources for hydrogen gas production. Conversion of biomass to hydrogen is potentially an economically viable opportunity to generate H<sub>2</sub> while utilizing domestically available resources. The SR of biomass and biomass-derived materials has been considered as an alternative source of renewable energy. The most commonly used techniques for biomass reforming are gasification and pyrolysis. Biomass pyrolysis, in which biomass is heated and decomposed in an inert atmosphere or under vacuum, has been reviewed by Antal [27,28]. Pyrolysis of cellulosic carbohydrates leads to variety of smaller compounds, including liquid organics, light gases, and char. Pyrolysis of glucose and subsequent steam reforming of fast-pyrolysis oil has been investigated for the production of hydrogen gas at 550-810 °C using Ni based catalyst [29]. The disadvantage of pyrolysis is the decomposition of the feedstock, resulting in the formation of char. Pyrolysis of biomass produces bio-oil and glycerol, which can subsequently be used in SR to obtain hydrogen. Steam gasification of cellulose, lignin, and bagasse has been reported at 700 °C [29], and the effect of the heating rates on the formation of the char has been studied. It was reported that there is no pronounced influence of heating rate on the elemental composition of char, but higher rates substantially increased the reaction rate of char. Gasification of glucose in supercritical water at 600 °C, 34.5 MPa, and 30 s residence time results in formation of the H<sub>2</sub>, CO<sub>2</sub>, CO, and CH<sub>4</sub>. Alternatively, hydrogen can be directly obtained from aqueous-phase reforming (APR) of glucose without formation of char. The APR reactions of glucose were only successful at very low concentrations of glucose (1%), whereas high biomass concentration will be necessary to reach commercial goals [29].

### 3.3. Hydrogen Market

The markets partly define the requirements for the production technologies as well as potential partners to commercialize new hydrogen production technologies. It has been reported that 50 million tonnes of hydrogen are traded annually worldwide with a growth rate of nearly 10% per year for the time being [30]. It is primarily used as a feedstock in the chemical industry, for instance, in the



manufacture of ammonia and methanol, and in refinery reprocessing and conversion processes. However, with the environmental regulations becoming more stringent, there is now growing interest in the use of hydrogen as an alternative fuel.

Hydrogen is considered as a viable alternative fuel and “energy carrier” of future. It can easily be used in fuel cells for production of electricity for stationary applications and mobile electric vehicle operations. However, the demand on hydrogen is not limited to utilization as a source of energy. Hydrogen gas is a widely used feedstock for the production of chemicals, hydrogenation of fats and oils in food industry, production of electronic devices, processing steel and also for desulfurization and re-formulation of gasoline in refineries.

### **3.3.1. Transport**

Today's transportation system depends upon liquid fuels (gasoline, diesel, and jet) because of their high energy density by weight and volume and their ease of use. The world is exhausting its resources of the light crude oils used to make liquid fuels with consumption of oil exceeding discoveries of oil. The largescale drilling into all the world's sedimentary basins (except Antarctica) where oil is found supports the perspective that it is unlikely that new major oil providences will be found. There are many alternative transport fuel futures. Almost all of the options require the large-scale use of hydrogen. These options have been defined into three broad categories based on how the hydrogen is used: liquid fuels, CO<sub>2</sub>-free liquid fuels, and direct hydrogen fuels.

### **3.3.2. Industrial Market**

There are thousands of industrial users of hydrogen. Most users use relatively small quantities. However, there are three industrial markets where the facility size matches the output of centralized high-volume hydrogen production systems.

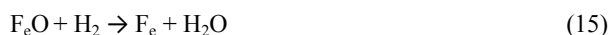
#### **3.3.2.1. Ammonia**

Ammonia production (fertilizer) consumes about half the hydrogen produced today and is the primary chemical industry use of hydrogen. All nitrate fertilizers require hydrogen in their production processes. Ammonia is currently made where there is inexpensive natural gas that provides inexpensive hydrogen and shipped to the customer. The low cost of shipping ammonia favors very large ammonia production plants with very large demands for hydrogen.



### 3.3.2.2. Direct Reduction of Iron Ore

In the production processes for converting iron ores into iron and steel, carbon, primarily in the form of coke, has been traditionally used to reduce the iron oxides to iron metal. However, in the last several decades, there has been increasing production of iron using the direct reduction iron (DRI) process. In the DRI process, syngas (a mixture of H<sub>2</sub> and CO) made from natural gas is used to reduce iron ores to iron. The major chemical reactions are as follows:



The DRI process has lower capital costs than alternative methods used to produce iron but requires a low-cost source of hydrogen. The primary market for DRI is to provide a purified iron feed for electric arc furnaces (EAFs) that produce various steel products. Iron production is potentially a significant existing market for hydrogen. If low-cost hydrogen were available, the DRI process would replace other methods of iron production. The economics of DRI relative to other processes (and the potential demand for hydrogen) depend upon the continuing improvements in EAF technology in terms of reduced production costs and increased capabilities to produce higher-quality steel that, in turn, creates the demand for more high-purity iron by the DRI process as traditional sources of scrap metal are exhausted.

### 3.3.2.3. Petrochemical

The use of H<sub>2</sub> in the chemical and petroleum refining industries is of prime importance. Hydrogen is essentially a hydrogenating agent. Hydrogen use in the petroleum refining includes many processing schemes such as hydrocracking, hydrofinishing of lube oils, hydrodealkylation and hydrodesulfurization of petroleum fractions and residues. Hydrocracking of petroleum resids is becoming more important to produce lighter petroleum distillates of low sulfur and nitrogen content to meet stringent government-mandated product specifications to control pollution. In the petrochemical field, hydrogen is used to hydrogenate benzene to cyclohexane and benzoic acid to cyclohexane carboxylic acid. These compounds are precursors for



nylon production. It is also used to selectively hydrogenate acetylene from C4 olefin mixture [31].

### 3.3.3. Intermediate and Peak Electricity Production

The demand for electricity varies daily, weekly, and seasonally. As a result, the market price of electricity varies by an order of magnitude as a function of time. To meet this demand, the utilities buy lower-capital-cost peaking power units, typically gas turbines that burn natural gas. In addition, utilities have developed storage devices so that they can buy electricity during times of low demand and low cost and sell the electricity during times of high demand and high prices. The variability of the price of electricity creates the potential for a large hydrogen market aimed at producing electrical power at those times of day when the price of electricity is at its maximum. A hydrogen intermediate and peak electrical system (HIPES) has been proposed by Charles Forsberg [32,33] that consists of three components:

- **Hydrogen production:** A power plant unit with an associated hydrogen and oxygen production plant to produce  $H_2$  and  $O_2$  at a constant rate to minimize the production costs.
- **Hydrogen storage:** One or more underground facilities for the low-cost storage of hydrogen and oxygen (optional). Underground caverns, depleted oil and gas fields, and aquifers are the traditional approaches to the low-cost storage of natural gas to meet seasonally variable natural gas demand. Underground storage is the only known low-cost technology for storing compressed gases; however, the storage economics demand very large facilities. This storage characteristic favors large-scale centralized hydrogen production.
- **Peak electric production:** Large banks of FC (or other systems) convert hydrogen to electricity during periods of high demand for electrical power and associated high prices for electricity. For every megawatt of steady-state hydrogen production, there would be several megawatts of FC.

While hydrogen is produced at a constant rate, the fuel-cell electrical production is highly variable—from zero to many times the rate of energy production from the reactor when the price of electricity is high. The economic feasibility of HIPES is based on: (1) the lowcost of large-scale bulk storage of hydrogen and (2) projected costs and efficiencies of fuel cells or other technologies to convert hydrogen to electricity. HIPES, as an electric energy



storage system, has the unique capability to economically store very large quantities of energy as compressed hydrogen over periods of weeks or months to address weekly and seasonal variations in electric demand. This is not a viable option all kinds of peak electric systems such as pumped hydro systems where the cost of energy storage over time becomes excessive. HIPES, if successful, may be an enabling technology for a nuclear-H<sub>2</sub> renewables economy. The fundamental problem for large-scale use of renewables is to match electricity production to electricity demand. Were there no electricity storage problem, wind or solar would become economic wherever their production cost is below the price of electricity, not the cost of electricity plus energy storage. HIPES may be an enabling technology to meet electricity demand when a significant fraction of the electricity is produced with renewables and the renewable electrical output does not match the consumer demand. The ability to economically store hydrogen for days, weeks, or months provides a bridging mechanism for the large variability of many renewable energy sources [34].

#### **3.3.4. Commercial Markets**

Hydrogen is being considered for commercial applications in buildings with the co-production of electricity and heat. If highly economic hydrogen production is achieved, hydrogen may be used to generate electricity, hot water, building heating, and building cooling. This is a distributed market with relatively small hydrogen consumption in individual facilities. This market does not favor large-scale hydrogen production techniques.

#### **3.3.5. Fuel Cells**

Nowadays catalytic SR is a new interest focus as the main pathway to obtain hydrogen from hydrocarbons or alcohols to be supplied to a fuel cell [35]. FC are electrochemical devices that convert the chemical energy of a reaction directly into electrical energy. The basic physical structure or building block of a fuel cell consists of an electrolyte layer in contact with a porous anode and cathode on either side. A schematic representation of a fuel cell with the reactant/product gases and the ion conduction flow directions through the cell is shown in Figure 1. In a typical FC, hydrogen is fed continuously to the anode (negative electrode) compartment and an oxidant (i.e., oxygen from air) is fed continuously to the cathode (positive electrode) compartment; the electrochemical reactions take place at the electrodes to produce an electric current.

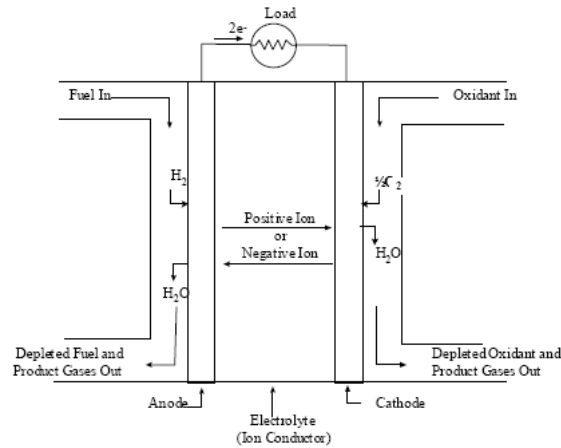


Figure 1: Schematic of an Individual Fuel Cell

FC are an important technology for a potentially wide variety of applications including micropower, auxiliary power, transportation power, stationary power for buildings and other distributed generation applications, and central power. These applications will be in a large number of industries worldwide [36].

For stationary applications, natural gas is the fuel of choice due to its availability and ease in distribution. For automotive applications, gasoline is the most convenient fuel since it can be easily transported. However, PEMFCs are very sensitive to impurities in fuel and have a sulphur specification less than 1 ppm. Gasoline has a 30 ppm sulphur standard in USA while hydrogen from coal gasifiers may contain 100–200 ppm sulphur [26].

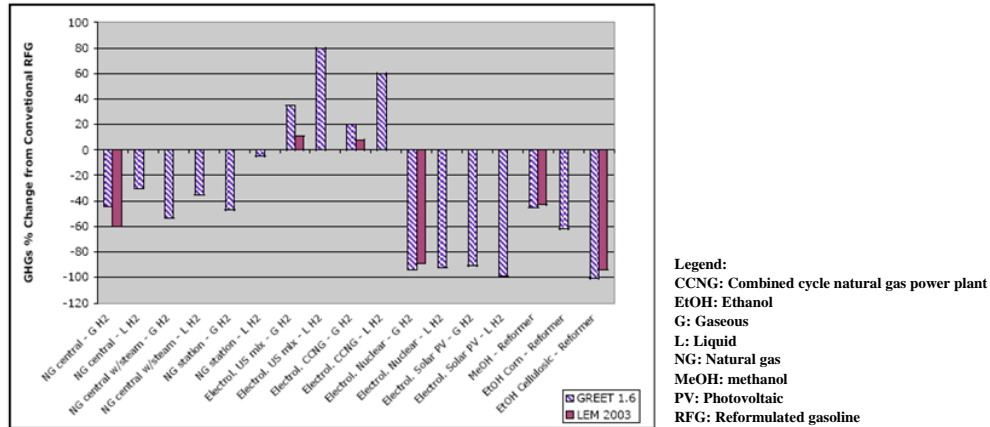


## 4. ENVIRONMENTAL IMPACTS OF HYDROGEN PRODUCTION

Additional important considerations for potential hydrogen production methods other than costs and feedstock requirements include the environmental implications of various hydrogen production methods. These considerations include not only global warming emissions, but also local pollutant emissions, soil and water quality impacts, and land, water, and other non-feedstock resource requirements. The global warming and air pollutant impacts of various hydrogen production pathways have been reasonably well-studied, at least for the most prominent potential production pathways, but other environmental considerations have been less well characterized. Additional studies are needed to better characterize the potential environmental impacts of hydrogen production—both generally and in terms of impacts on specific regions.

### 4.1. Greenhouse Gas Emissions Estimates from Hydrogen Fuel Pathways

Various hydrogen production strategies have dramatically differing implications with regard to the greenhouse gas emissions (GHG) implications of end-use. The Figure 2 as shown below compares estimated full fuel-cycle global warming emissions of several combined hydrogen production and distribution pathways, assuming that hydrogen is used to operate a vehicle in comparison with using reformulated gasoline (RFG) in conventional vehicles. The results were obtained by two well-known GHG analysis models, for various hydrogen production and distribution pathways. These models are the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) Model developed by Argonne National Lab (ANL, 2001), and the Lifecycle Emission Model (LEM) developed at UC Davis. The figure shows that different hydrogen production pathways have dramatically different effects on global warming emissions. Depending on the hydrogen production and distribution pathway, emissions can be as high as 80% of the level of emissions from conventional vehicles (using the U.S. average grid power mix to produce liquid hydrogen via electrolysis), and as low as 0% with biomass and some other renewable pathways. If one goal of the use of hydrogen is to reduce GHG emissions, then the method of hydrogen production and distribution chosen is clearly critical to achieving that goal. Figure 2 does not, however, address an additional, important consideration in weighing the relative global warming benefits of renewably-produced hydrogen: that is, whether renewable energy would instead be better used to displace other sources of electricity [37].



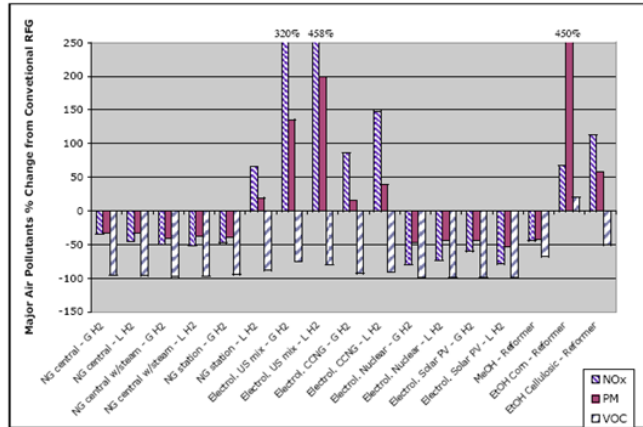
Source: Argonne National Lab (ANL, 2001), Delucchi, 2003

Figure 2: Relative fuel-cycle greenhouse gas emissions of H<sub>2</sub> fuel pathways

#### 4.2. Air Pollutant Emissions and Soil and Water Impacts from Hydrogen Fuel Pathways

Air pollutant emissions and soil and water impacts of hydrogen production and distribution pathways also can vary widely for various methods and, unlike GHG emissions, have important local and regional environmental quality implications. These impacts have generally been studied in less detail than potential GHG emissions, particularly with regard to soil and water impacts. The social and environmental welfare impacts of air pollutant emissions also vary in part depending on population exposure levels, adding even more uncertainty with regard to these potential impacts. Figure 3, below, presents an analysis of major air pollutant emissions from the same hydrogen production and distribution pathways shown in Figure 2. As before, the comparison is between a vehicle operating on a hydrogen fuel cell and a vehicle operating on reformulated gasoline. Shown are total pollutant emissions of NO<sub>x</sub>, fine particulate matter less than 10 microns in diameter (PM), and volatile organic compounds (VOC) from the full fuel cycle for each pathway.

As shown in the figure 2, the relative air pollutant emissions from transportation uses of hydrogen also vary widely depending on the hydrogen production pathway. The figure suggests that most hydrogen production pathways produce significant air quality benefits with significant reductions but some – particularly electrolyzer pathways coupled with either average grid mix or combined cycle natural gas plants – producing significant increases in NO<sub>x</sub> and particulate matter (PM) emissions [37].



Source: Argonne National Lab (ANL, 2001), Delucchi, 2003

Figure 3: Air pollutant emissions from H<sub>2</sub> fuel cell vehicle refueling pathways

These results changes at times when renewable energy is available but not in a position to displace conventional power generation. Wind power, for example, is sometimes available during off-peak hours when the marginal system generator is a baseload power plant. In these instances, using excess wind power that cannot be absorbed by the grid to produce hydrogen for vehicles would result in additional pollution benefits, regardless of the theoretical advantages of displacing conventional power generation. Hydrogen production under these circumstances provides a form of energy storage that can help to offset the limitations of intermittent renewable resources from a grid perspective.

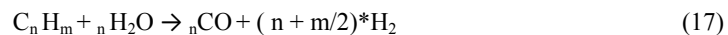
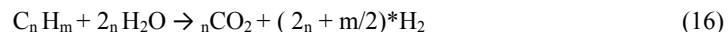


## 5. GENERAL PRINCIPLES OF STEAM REFORMING

Most hydrogen production occurs by SR; is the oldest and most widely used technology: converting a hydrocarbon–steam mixture into a mixture of (primarily) H<sub>2</sub> and CO<sub>2</sub>. Steam reforming is achieved by reaction over a catalyst at high temperature. In addition to the energy required to provide the steam, the overall reaction is endothermic, so energy must be added to drive it. As heat must be supplied to the system, the process must burn either a second fuel, a fraction of the primary fuel, or the residual fuels that remain in the reformat stream. This last option is often done in practice to recover heating value that would otherwise be wasted [31].

The first step of the process is the reforming. This reaction is carried out in the range of temperatures 673–1273 K. Reforming can be either by steam (steam reforming), or by humidified air (partial oxidation reforming), or by a mixture of air and steam (auto-thermal reforming). Compared with partial oxidation and autothermal reforming, catalytic steam reforming offers higher hydrogen concentrations. The steam reforming reaction, on the other hand, is a highly endothermic reaction and requires heating. Another disadvantage is its slow start-up, which makes it more suitable for a stationary system rather than a mobile system [38]. Here, attention is focus on the SR reaction.

The stoichiometry of hydrocarbon reforming for maximum hydrogen production is described by Eq. (16). This reaction is the sum of two reactions (Eqs. (17) and (18)) that take place simultaneously in any reformer.



The initial steps in steam reforming are dissociative adsorption of the hydrocarbons on the metal sites of the catalyst and reaction of the adsorbed C<sub>x</sub>H<sub>y</sub> species with adsorbed H<sub>2</sub>O-derived species to produce CO and H<sub>2</sub> (Eq. (17)). With an active catalyst at temperatures below 600°C, reforming of naphtha (Eq. (17)) is irreversible, with no intermediates, and the only byproduct is carbon that forms on the catalyst [38]. The reversible reactions are the water-gas shift (WGS) reaction (Eq. (18)), the methanation reaction (Eq. (19)), and the disproportionation of CO (Eq. (20)), which are equilibrium limited. Only at higher temperatures does thermal cracking of the hydrocarbon itself compete with the catalyzed reactions. Because natural gas and naphthas have been the main feedstocks in commercial steam reforming processes that produce of hydrogen and synthesis gas (a mixture of hydrogen and carbon monoxide).



The reformed fuel often contains other gases such as CO. Except for use in high temperature fuels cells (HTFC), the CO concentration must be reduced to a very low level (around 10 ppm). Various options for CO reduction include water–gas shift (WGS), preferential oxidation of CO, methanation, membrane separators and combinations of these with the reforming reactor [39]. In essence, reforming a fuel consists of the following steps:

- Feedstock purification (including sulfur removal).
- Steam reforming of feedstock to form hydrogen and carbon oxides.
- Primary purification—conversion of carbon monoxide to carbon dioxide.
- Secondary purification—further reduction of carbon monoxide.

Normally, a WGS process is chosen as primary purification. In the WGS, carbon monoxide is reacted with steam to give CO<sub>2</sub> and H<sub>2</sub>. The reaction is exothermic and independent of pressure. Commonly It consist in a two steps process, high temperature and low temperature water gas shift (HTS and LTS), that increase the H<sub>2</sub>:CO ratio and, consequently, reduce the CO content of this gas stream. The residual CO can be then reduced further to ppm level in a CO preferential oxidation (PROX) reactor as a second purification. In order to maximize the hydrogen yield, an excess of water is usually fed to carry out the water gas shift reaction.

Exit gases from the shift conversion are treated to remove carbon dioxide. This may be done by absorbing carbon dioxide in a physical or chemical absorption solvent or by adsorbing it using a special type of molecular sieves. Carbon dioxide, recovered from the treatment agent as a byproduct, is mainly used with ammonia to produce urea.

### 5.1. Operation Parameters

The important process variables are reactor temperature, residence time, catalyst and steam/carbon ratio. Feed characteristics are also considered, since they influence the process severity.



### 5.1.1. Ratio Steam:Carbon

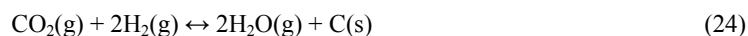
An additional advantage of using a larger than stoichiometric quantity of steam is that it enhances hydrocarbon conversion due to the lower partial pressure of hydrocarbons.

### 5.1.2. Catalyst

The catalysts generally used in catalytic reforming are dual functional to provide two types of catalytic sites, hydrogenation-dehydrogenation sites and acid sites. The former sites are provided by platinum, which is the best known hydrogenation-dehydrogenation catalyst and the latter (acid sites) promote carbonium ion formation and are provided by an alumina carrier (besides the fact that presents some problems at low temperatures such as fast sinters). The two types of sites are necessary for aromatization and isomerization reactions. Bimetallic catalysts such as Pt/Re were found to have better stability, increased catalyst activity, and selectivity. Trimetallic catalysts of noble metal alloys are also used for the same purpose. The increased stability of these catalysts allowed operation at lower pressures. Reforming units can perform similarly with higher coke levels (20–25% versus 15–20%). These catalysts can tolerate higher sulfur naphtha feeds (>1 ppm). Higher profitability may be realized by increasing the cycle length.

### 5.1.3. Coke Formation

The main reactions may be accompanied by coke formation. Coke may be formed due to the decomposition of methane (eq. 21) or CO, the Boudouart reaction (eq. 22), or the reaction of CO<sub>2</sub> or CO with H<sub>2</sub> (eqs. 23,24) [40]. The possible reactions that can be attributed to carbon formation are given as follows:



Another possible route for the formation of carbon is through ethylene:





Carbon formation in steam reformers must be prevented for two main reasons: Carbon deposition on the active sites of the catalyst which leads to several undesirable reactions and products affecting the purity of the reformation products like loss of effective surface area, lower the heat transfer rate from catalyst to gas, and plug of the void space within the catalyst. Secondly, carbon deposits grow that large that can cause total blockage of the reformer tubes, resulting in the development of “hot spots” [41]. Carbon formation reactions can be minimized by adding excess steam.



## 6. STEAM REFORMING OF HYDROCARBONS

The most economical way to produce hydrogen is by steam reforming of petroleum fractions and natural gas. In this process, two major sources of hydrogen (water and hydrocarbons) are reacted to produce a mixture of synthesis gas. Hydrogen can then be separated from the mixture after shift converting CO to CO<sub>2</sub>. Carbon oxides are removed by passing the mixture through a pressure swing adsorption system.

The reaction is a catalytic process that typically takes place in vapour phase at atmospheric pressure and temperatures around 1073 K. Catalysts for steam reforming of hydrocarbons are mainly based on nickel as active component supported on oxides with high thermal stability [31]. Although noble metals (Ru, Rh, Pt) are more effective for the SR of hydrocarbons than Ni and less susceptible to carbon formation, such catalysts are not common in industrial applications because of their cost [42].

The feed to the shift converter contains large amounts of carbon monoxide which should be oxidized. An iron catalyst promoted with chromium oxide is used at a temperature range of 425–500°C to enhance the oxidation. The product is a pure hydrogen gas containing small amounts of carbon monoxide and carbon dioxide.

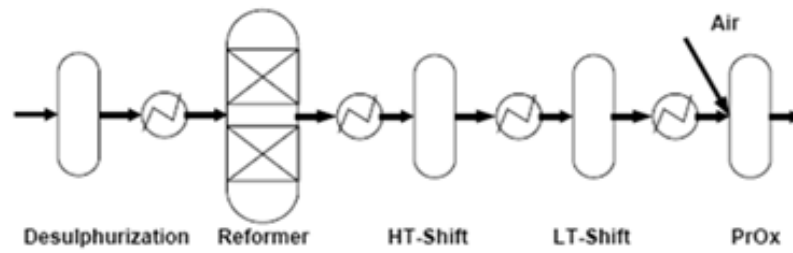
The main advantage of reforming fossil fuels is that it is a mature technology that uses existing fuel infrastructures. It reduces the need to transport and store hydrogen. It is the less expensive process than other hydrogen production methods. Comparing to electrolysis, do not need the input of large amounts of energy.

The disadvantages are usually associated with the reformers. They are complex, large and expensive, can have relatively long warm-up times and can introduce additional losses into the energy conversion process, especially those that have small thermal mass. In terms of contamination, the pollution generated by reformers take three forms: CO<sub>2</sub> emissions, incomplete reactions, leaving carbon monoxide and some of the source fuel in the reformat and production of pollutants through combustion, such as nitrous oxides.

The design of the steam reforming process of CH<sub>4</sub> is explained referring to figure 4 where the main reactions of each conversion are subscribed. First, natural gas is desulphurized in, e.g. impregnated active carbon at room temperature from natural sulphur and odorizers. After blended with water in a molar ratio of 3 the mixture reacts over a catalyst at 800 °C. The dry composition of the reformat gas is about 77% hydrogen, 15% carbon monoxide and 8% carbon dioxide. Methane can be reduced to 0.4%. During the following water–gas-shift reactions the CO-contents can be converted



to less than 1% before the residual catalyst-poison is removed in a preferential oxidation unit consuming a stoichiometric air-ratio of 2.



Source: [31]

Figure 4: Principles scheme of a steam reforming process.



## 7. STEAM REFORMING OF ETHANOL

Although several sources of hydrogen have been investigated, alcohols, and in particular ethanol, which is a renewable material easily obtained from biomass, might be considered as a good choice, especially for Latin American countries with extensive plantations of sugar cane and corn. Ethanol is easier and safer to store and transport due to its low toxicity and volatility, and for being biodegradable. Ethanol presents several advantages related to natural availability, storage and handling safety. It can be produced renewably from several biomass sources, including energy plants, waste materials from agro industries or forestry residue materials, organic fraction of municipal solid waste, etc [43-46].

In addition, the bio ethanol-to-hydrogen system has the significant advantage of being nearly CO<sub>2</sub> neutral, since the carbon dioxide produced is consumed for biomass growth, thus offering a nearly closed carbon loop while the use of methanol and gasoline adds to CO<sub>2</sub> emissions. Thus, the use of ethanol will not contribute to global warming.

Bio-ethanol, which is a dilute aqueous solution containing around 12% (wt.) ethanol, could be directly subjected to steam reforming thereby eliminating one unit operation of distillation required to produce pure ethanol [10]. Since water is also consumed during its conversion into hydrogen, there is no need for absolute ethanol to be produced as it would be required if it were to be used in conventional engines, either alone or mixed with gasoline. Both reactants (water and ethanol) includes hydrogen atoms that contribute to the total yield and the thermal efficiency obtained is considerably good (>85%) [35]. The entire process could therefore be economically attractive.

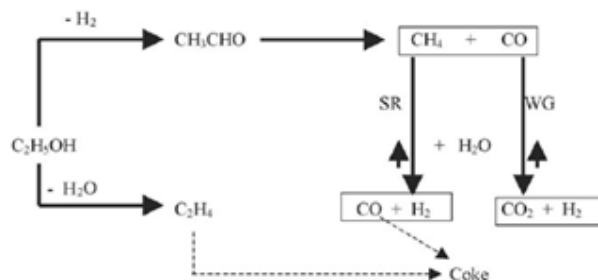
The first step in the conversion of ethanol to hydrogen is reforming. The bioethanol steam reforming is an endothermic reaction carried out in the range of temperatures 673–1273 K, for this reason the necessary heat has to be supplied from an external source; it could be represented in the simplest case by the following stoichiometry equation:



In fig 5 it is proposed a reaction mechanism for ethanol steam reforming. As per this scheme, ethanol is first dehydrogenated to acetaldehyde which subsequently decomposes to CH<sub>4</sub> and CO. These lead to the formation of H<sub>2</sub> and CO<sub>2</sub> by steam



reforming and water gas shift (WGS) reactions. Thus, the exit stream composition is governed by  $\text{CH}_4$  steam reforming and WGS reactions [10].



Source: [10]

**Figure 5: Reaction mechanism for steam reforming of ethanol**

Ethanol has relatively high hydrogen content; the key aim of this process is to maximize  $\text{H}_2$  production, discouraging at the same time side reactions as ethanol dehydration and decomposition that lead to produce undesirable products, such as methane, diethyl ether or acetic acid that compete for hydrogen atoms [46], which causing the reduction of the global yield; because of this the use of stable and selective catalytic formulations is an important issue for the process development [35]. In addition, the formation of large amounts of  $\text{CO}$  reduce the global yield of the reaction and would require a complex gas clean up process downstream in case of feeding into the fuel cell. In summary, among the various processes and primary fuels that have been proposed in the production of hydrogen, steam reforming of ethanol is the most attractive.

### 7.1. Thermodynamics Considerations

Thermodynamic aspects of ethanol steam reforming have received a fair amount of attention in the published literature. The process has been shown to be entirely feasible from a thermodynamic point of view [41]. Spite of the apparent simplicity of the stoichiometry reaction for maximum hydrogen production, the reaction pathway during ethanol steam reforming comprises a complex series of simultaneous reactions, which are more or less promoted depending on the nature of the catalyst. The reaction is strongly endothermic and produces only  $\text{H}_2$  and  $\text{CO}_2$  if ethanol reacts in the most desirable way. However, other undesirable products such as  $\text{CO}$  and  $\text{CH}_4$  are also usually formed during reaction. Aupretre et al. [47] have discussed the main reactions in ethanol steam reforming that account for the formation of these by-products. The table 2 show the main reactions involved in the catalytic steam reforming of ethanol; those include ethanol dehydration to ethylene,



ethanol cracking into methane, carbon monoxide and hydrogen, ethanol dehydrogenation into acetaldehyde, acetaldehyde decarbonilation, ethanol decomposition into acetone, formation of acetic acid, steam reforming of ethanol, acetaldehyde, acetone, acetic acid, ethylene and methane, and the water gas shift and methanation reactions.

**Table 2: Main mechanism involved in the catalyst steam reforming of ethanol**

Decomposition reactions		
Ethanol	$\text{CH}_3\text{CH}_2\text{OH} \rightleftharpoons \text{CH}_3\text{CHO} + \text{H}_2$ $\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O}$ $\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CO} + \text{CH}_4 + \text{H}_2$ $\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2$	Dehydrogenation Dehydration Cracking Oxidation
Acetaldehyde	$2\text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{COCH}_3 + \text{CO} + \text{H}_2$ $\text{CH}_3\text{CHO} \rightarrow \text{CO} + \text{CH}_4$	Acetone formation Decarbonilation
Acetic	$\text{CH}_3\text{COOH} \rightarrow \text{CO}_2 + \text{CH}_4$	Decarboxilation
Ethylene	$\text{CH}_2=\text{CH}_2 \rightarrow 2\text{C} + 2\text{H}_2$	Carbon deposition
Methane	$\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$	Carbon deposition
Carbon monoxide	$2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$	Carbon deposition
Steam reforming reactions		
Ethanol	$\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow 2\text{CO} + 4\text{H}_2$	
Acetaldehyde	$\text{CH}_3\text{CHO} + \text{H}_2\text{O} \rightarrow 2\text{CO} + 3\text{H}_2$	
Acetic	$\text{CH}_3\text{COOH} + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 4\text{H}_2$	
Acetone	$\text{CH}_3\text{COCH}_3 + 2\text{H}_2\text{O} \rightarrow 3\text{CO} + 5\text{H}_2$	
Ethylene	$\text{CH}_2=\text{CH}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{CO} + 4\text{H}_2$	
Methane	$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$	
Carbon monoxide	$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$	Water gas shift
Carbon	$\text{C} + \text{H}_2\text{O} \rightleftharpoons \text{CO} + \text{H}_2$	Carbon gasification

Source: [62]

Therefore the selectivity to hydrogen is affected by many undesirable side reactions, the yield of hydrogen also depends on the process variables such as, temperature, reactants ratio, space time, etc. and obviously, on the catalytic composition. In order to design an effective catalyst for maximizing the yield of hydrogen, it is necessary to know the effect of these variables on product distribution, and from these results it is possible to propose the reactions scheme involved.

Results in increase in number of moles, increasing the temperature and lowering the pressure are in favor of ethanol reforming. At 500 K, steam reforming of ethanol does not occur ( $\Delta G > 0$ ). However, ethanol decomposition can easily occur at this temperature since the value of  $\Delta G$  is sufficiently negative. In fact, ethanol decomposition to  $\text{CO}_2$  y  $\text{CH}_4$  is strongly favored at low temperatures (<473 K). Garcia and Laborde [41] found that higher temperatures and water-to-ethanol ratios are needed to obtain the best  $\text{H}_2$  production from ethanol. They examined the thermodynamic equilibrium of this system and suggested operation at  $T > 650$  K, atmospheric pressure and a water-to-ethanol molar ratio of up to 10 in the feed to maximize  $\text{H}_2$  production, minimize the formation of  $\text{CO}$  and  $\text{CH}_4$  and avoid carbon deposition on the catalyst.



Vasudeva et al. [48] found that H<sub>2</sub> yields as high as 5.5 mol/mol of ethanol in the feed can be obtained at equilibrium at temperatures around 773–873K with water-to-ethanol molar ratios of above 20. Aupretre et al. [47] have also performed a thermodynamic analysis of the system. They have further shown that an increase in the total pressure leads to a decrease in the H<sub>2</sub> and CO yields while the equilibrium composition in CH<sub>4</sub> increases.

Fishtik et al. [49] found that for temperatures at or above 700–800K and for high water-to-ethanol ratios, the desired reaction of ethanol steam reforming is predominant and the formation of CO and CH<sub>4</sub> is minimized. At high temperatures (>1073 K), the equilibrium H<sub>2</sub> selectivity is nearly 100%. In a more recent study, Mas et al. [50] suggested that while high temperatures and high water-to-ethanol ratios favor H<sub>2</sub> production, low temperatures and high water-to-ethanol ratios are suitable to minimize CO formation. At a water-to-ethanol molar ratio of 3, temperatures higher than 500K are required to avoid coke formation. Freni et al. [51,52] carried out a thermodynamic analysis of the ethanol–water system as applied to an MCFC and suggested that a high water-to-ethanol ratio in the feed reduced the yield of undesirable products such as CO, CH<sub>4</sub> and carbon. In another study, Thoeophilus [53] reported a H<sub>2</sub> yield of nearly 100% at 1000 K, atmospheric pressure and a water-to-ethanol molar ratio of 5.

## 7.2. Kinetic Considerations

There are a little information referred to the general kinetic pattern and reaction mechanism involving this reaction scheme. In this sense Therdthianwong et al. [54] deduced a power law equation, Eqs. (27) fitted to an experimental data obtained on a commercial catalyst (Ni/Al<sub>2</sub>O<sub>3</sub>) and valid for 1 atm and 673 K:

$$r_1 = k_{ap} P_E^{2.5} P_A^9 \quad (27)$$

where  $k_{ap} = 280,075$

Where  $P_E$  and  $P_A$  are the partial pressures of ethanol and water, respectively (atm) and  $K_{ap}$  is the reaction constant (mol/g cat h atm<sup>9.52</sup>). The use of a similar catalyst for the crude bioethanol steam reforming was recently analyzed by Akande et al. [55], in this case the kinetic pattern was adjusted according to an Eley-Rideal mechanism being the controlling step, the reaction between the adsorbed bioethanol molecules and the steam at the bulk gas, Eq. (28). The same paper reported another model based in a power law type equation Eq. (29), however, both expressions are adjusted supposing that the reaction takes place according to a single step.



$$r_2 = 3,12 * 10^{-2} e^{(-7560/RT)} N_A^{0,43} \quad (28)$$

$$r_3 = \frac{2,08 * 10^3 e^{(-4430/RT)} N_A}{(1+3,83*10^7 N_A)^2} \quad (29)$$

Where  $N_A$  represent the bioethanol molar flow (kmol/s) and  $r_{2,3}$  are the reaction rate (kmol/kgcat s). Although these equations have a great practice sense, their use to develop robust models that allow to analyze thoroughly the process are restricted. L.E. Arteaga et al. [35] proposed a system of equations able to describe the kinetic mechanism. The developed models are used to obtain a new bioethanol steam reformer prototype, using the analogy between tubes and shell heat exchangers and fixed bed multitube reactors.

### 7.3. Factors Controlling Selectivity for ethanol steam reforming

#### 7.3.1. Nature of the Catalyst

The development and testing of catalysts suitable for ethanol steam reforming has been recently reviewed [55-61]. Nowadays, there are no commercial catalysts for ethanol steam reforming, because most catalysts used for these applications suffer from deactivation problems due to carbon deposition on the active phase. Thus, the formulation of a new catalyst able to overcome the operational problems is the first goal.

Several catalysts have been proposed which show sufficient activity and stability to be further considered for practical applications. Although many noble metals (Rh/Al<sub>2</sub>O<sub>3</sub>, Pt/Al<sub>2</sub>O<sub>3</sub>, Pd/Al<sub>2</sub>O<sub>3</sub>, Ru/TiO<sub>2</sub>, Rh/CeO<sub>2</sub>-ZrO<sub>2</sub>) and non-noble metals (Ni/Al<sub>2</sub>O<sub>3</sub>, Cu/Al<sub>2</sub>O<sub>3</sub>, Fe/Al<sub>2</sub>O<sub>3</sub>, Ni/Al<sub>2</sub>O<sub>3</sub>, Ni/ La<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>, Ni/Y<sub>2</sub>O<sub>3</sub>, Co/Al<sub>2</sub>O<sub>3</sub>, Co/SiO<sub>2</sub>) on different supports have been shown to be active in this process, Ni seems to be the preferred active ingredient because of its high activity and low cost [47,55].

The catalytic performance of supported noble metal catalysts (Rh, Ru, Pt, Pd) for the steam reforming of ethanol has been investigated by Liguras et al. [56] in the temperature range of 600–850 °C. They studied the effect of the nature of the support (Al<sub>2</sub>O<sub>3</sub>, MgO, TiO<sub>2</sub>) and the metal loading (0–5%) on the reforming reactions. For low-loaded catalysts, compared to Ru, Pt and Pd, Rh was found to be significantly more active and selective towards hydrogen.



The transition metals also have a special interest because of their profitability and stability in the reforming processes. A number of Ni-based catalysts supported on different oxides have been reported as very active and selective for the steam reforming of bioethanol; Ni has high activity in steam reforming promoting C—C bond rupture in acetaldehyde.

In previous works [44,46,57], Ni dispersed on La<sub>2</sub>O<sub>3</sub> offers a catalyst for steam reforming of ethanol which is not only active and selective toward hydrogen production but also stable with time on stream, even under conditions which favor carbon formation and deposition.

Frusteri et al. [58] studied SR of ethanol on undoped and doped Ni/MgO catalysts. The dopants used were Li, Na or K. At 650 °C, the Ni/MgO catalyst was stable for 700 h time-on stream and showed very high selectivity to H<sub>2</sub> and CO<sub>2</sub>. This catalyst showed low tendency to promote CO methanation and ethanol decomposition reaction. In addition, the coke formation was strongly depressed in the presence of basic carrier MgO. Li and Na promoted the NiO reduction but negatively affected the dispersion of Ni/MgO catalyst, whereas K did not significantly affect either the morphology or the dispersion. Li and K enhanced the stability of Ni/MgO mainly by depressing Ni sintering.

The effect of Co catalyst with different metal oxide supports has been examined by Llorca et al. [62]. They prepared catalyst containing 1 wt% Co on different supports (alpha-Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, ZnO, La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and Sm<sub>2</sub>O<sub>3</sub>). Among all catalysts studied, Co/ZnO catalyst exhibited comparatively better performance (conversion: 100%, selectivity up to 73.8% to H<sub>2</sub> and 24.2% to CO<sub>2</sub> was obtained at 723 K), but at this temperature lower yield of H<sub>2</sub> (5.1 mol/mol of EtOH reacted) compared to theoretical value (6 mol/mol of ethanol reacted) was obtained. On the other hand, over the catalyst the decomposition of ethanol to acetone was high. Many side products such as C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, and CH<sub>3</sub>CHO were obtained. Therefore, at the reaction temperature, reforming reaction was low and dehydration reaction was prominent.

A wide range of catalysts were tested by Aupretre et al. [47] by changing both the active phase (Rh, Pt, Pd, Ru, Ni, Cu, Zn, Fe) and the oxide support (Al<sub>2</sub>O<sub>3</sub>, 12% CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, CeO<sub>2</sub>-ZrO<sub>2</sub>, ZrO<sub>2</sub>). At 700 °C and atmospheric pressure, gamma-Al<sub>2</sub>O<sub>3</sub> supported Rh and Ni gave the best performance compared to Pt, Cu, Zn or Fe. For Rh catalysts, 1% Rh/gamma-Al<sub>2</sub>O<sub>3</sub> showed the highest selectivity (88%) while 1% Rh/CeO<sub>2</sub>-ZrO<sub>2</sub> exhibited the highest yield to



hydrogen. Similar results were obtained for Ni catalysts. They reported that activity in the SR reaction directly varies as degree of mobility of surface OH groups, and selectivity towards CO<sub>2</sub> is controlled by the activity in the water–gas shift (WGS) reaction. The ceria-based supports were highly active for the WGS reaction.

Recently, Zhang et al. [63] studied ceria-supported Co, Ir and Ni catalyst for SR of ethanol for hydrogen production. All the catalysts were active and selective for hydrogen production. Ir/CeO<sub>2</sub> catalyst was the most stable and did not show any appreciable deactivation for 300 h time-on-stream. This was attributed to the high dispersion of Ir due to the strong interaction with the CeO<sub>2</sub>, thereby reducing the sintering of the catalyst.

A new bioethanol catalyst developed by the Institute of Catalysis and Petro-chemistry (ICP-CSIC-Madrid-Spain) have demonstrated very high activity, with hydrogen production efficiencies close to thermodynamic predictions, 4.5 moles of hydrogen per mole of EtOH feed at the temperature and pressure under consideration (650–700 °C and atmospheric pressure). An excellent stability for more than 500 h in continuous operation and more than 4000 h for accumulated tests, without deactivation was observed [61].

### 7.3.2. Coke Formation

A major problem for ethanol steam reforming is the deposition of carbon on the catalyst surface. Catalyst coking strongly depends on the reaction conditions and the properties of the catalyst.

Ethylene is a known coke precursor and carbon formation is primarily attributed to its presence in the product stream. The deposition of carbon by ethylene polymerization, and therefore suitable catalysts require combinations of active components and supports that do not promote dehydration and ethylene formation, and that are capable of reforming ethylene efficiently. Ethanol, however, decomposes through homogeneous thermal cracking into ethylene and water at high temperature [62]. The requirement for reduced carbon deposition on the catalyst as well as considerations about materials of construction and mechanical designs for fuel processors have driven research for obtaining catalysts that can reform ethanol efficiently and selectively at moderate and even low temperature, from 300 to 550 °C. Vasudeva et al. [48] suggested that carbon



formation occurs only at low water-to-ethanol ratios ( $<2$ ) and low temperatures (883 K).

However, coke formation can be prevented if ethanol is instead dehydrogenated to acetaldehyde, which has a very low coking activity. Acetaldehyde thus formed can then be subjected to steam reforming.

### 7.3.3. Temperature

Thermodynamic studies [41,49,50] has shown that the steam reforming of ethanol is feasible for temperature higher than 500 K, being methane, carbon oxides and  $H_2$  the main products. From a constructive point of view, it would be desirable that the ESR worked at lower temperatures, but methane production increases when temperature decreases. It must be noted that the higher the methane production is, the lower hydrogen yield will be, since each mole of methane contains two moles of hydrogen. On the contrary, if the ERS operates at high temperatures, the heat consumed by this reactor will be higher, and so will be the stream fraction or fuel burned for this purpose.

Garcia and Laborde [41] and Vasudeva et al. [48] have earlier shown that an increase in temperature leads to an increase in the  $H_2$  and CO concentration and a decrease in  $CH_4$  concentration at equilibrium.

Cavallaro and Freni [50,58] have investigated the steam reforming of ethanol over supported oxide catalysts. They have concluded that  $CuO/ZnO/Al_2O_3$  exhibit a good activity and CO,  $CO_2$  and  $H_2$  were the main products obtained at temperatures above 630 K. Mariño et al. [44,45,46] have studied the effect of different copper loading on catalytic behavior of  $Cu/Ni/K/Al_2O_3$  catalyst. They have found an acceptable performance to hydrogen at low temperatures (573 K).

### 7.3.4. Water/Ethanol Feed Ratio (WEFR)

The influence of water/ethanol molar ratio on ethanol steam reforming process transfer: the change in the mixture composition (increment with the less volatile component) causes a direct increment of the boiling point and the total flow and these factors are directly proportional to the energy consumption (sensitive heat) in the heating, reforming and conditioning stages, respectively [35].



Kinetic studies claim that a high ethanol/water ratio in the feed improves the conversion in ESR and WGS. An increase in the amount of water also has the effect of increasing the extent of the WGS and methane SR reactions, which reduces the amount of the undesired products, CO and CH<sub>4</sub> [37]. A water to ethanol feed ratio greater than 3 is necessary in order to obtain hydrogen and prevent carbon formation [41]. Nevertheless, water evaporation consumes a significant amount of heat; the use of a water-to-ethanol ratio higher than stoichiometry results in increased enthalpy needs for water evaporation. Then, if this ratio increases, the system available power decreases because a higher process fraction will have to be burned. Hence, there is a trade-off between the hydrogen production and the heat consumed in water evaporation.



## 8. STEAM REFORMING OF GLYCEROL

In recent years, many studies have focused in the recovery of high quality glycerol by-product [64,65,66]. In this context, the glycerol may represent a potential source for hydrogen production. Glycerol can be efficiently converted in hydrogen by means of its catalytic reaction with steam. In the steam reforming of glycerin, synthesis gas that contains both carbon monoxide (CO) and hydrogen (H<sub>2</sub>) is produced. From syngas, methanol, which is used for methyl esterification of vegetable oils, can be produced using conventional technology and, as a result, 100% biomass-based bio-diesel fuel could be produced.

Steam reforming of glycerol for hydrogen production involves complex reactions. As a result, several intermediate byproducts are formed and end up in the product stream affecting final purity of the hydrogen produced. Furthermore, the yield of the hydrogen depends on several process variables, such as system pressure, temperature, and water-to-glycerol feed ratio (WGFR). The overall reaction of hydrogen production by steam reforming of glycerol is:



### Overall Reaction

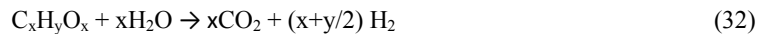


Recently, Simonetti et al [67] have reported a low-temperature (e.g., 550 K) catalytic process that converts into H<sub>2</sub>/CO gas mixtures. Because this production of synthesis gas can be accomplished in the same temperature range as Fischer–Tropsch synthesis, the endothermic production of synthesis gas at low temperatures can be coupled with exothermic Fischer–Tropsch synthesis, leading to an energy-integrated process for conversion of biomass to liquid transportation fuels.

The steam reforming of glycerol produces H<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>, and C, together with the unreacted water and glycerol. Only these compounds are the primary products formed in the reaction [68]. CH<sub>4</sub> competes against H<sub>2</sub>, and obviously CH<sub>4</sub> is not a desirable product in the case of H<sub>2</sub> production. Since the decomposition of glycerol to CH<sub>4</sub> is highly favorable during the reforming process, the catalyst must have sufficient capacity for reforming the produced CH<sub>4</sub> into hydrogen and carbon monoxide [69]. Carbon will cause deactivation of the catalyst and will be discussed later.



According to reaction 32, complete steam reforming of glycerol could provide a gas with a maximum hydrogen content of 70%, while reaction 33 suggests glycerol decomposition could lead to a hydrogen content of 57% [29].



A thermodynamic analysis of hydrogen production by steam reforming of glycerol was realized by Adhikari, S. et al [70] showing the feasibility of hydrogen production from glycerol steam reforming. Results show that the upper limit of the moles of hydrogen produced per mole of glycerol is 6 at 960 K, WGFR=9:1, and P =1 atm vs the stoichiometric value of 7.

### 8.1. Factors Controlling Selectivity for Glycerol steam reforming

#### 8.1.1. Nature of Catalyst

As the majority feedstock proposed in this work, there isn't a commercial catalyst to succeed over the conventional problems occurs in the SR. Czernik et al. [71,72] have produced hydrogen via steam reforming of crude glycerol using a commercial nickel based naphtha reforming catalyst (C11- NK). Nickel is the base catalyst for SR of hydrocarbons mainly for its high activity and low cost

Iriondo et al. [73] studied glycerol steam reforming over alumina-supported nickel catalysts modified with Ce, Mg, Zr and La. The catalytic activity of the samples studied in this work clearly indicated the different catalyst functionalities necessary to carry out the reaction.

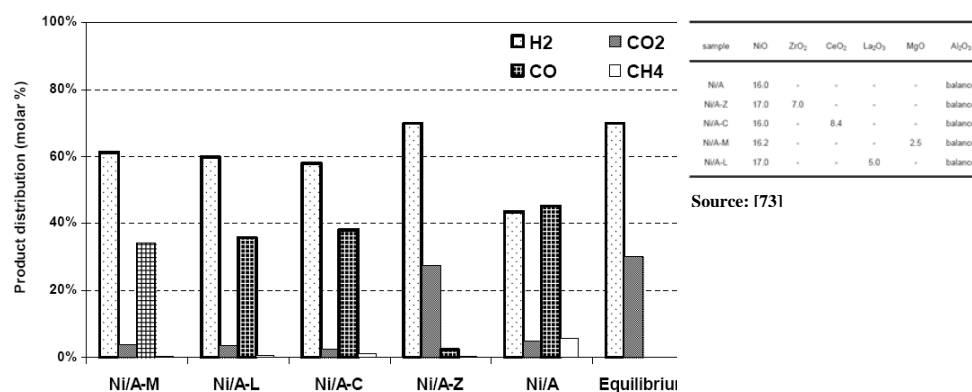


Figure 6: Product distribution for steam reforming of glycerol over Ni catalysts (T= 873 K, P=0.1 MPa, WHSV= 2.5 h<sup>-1</sup>)



In a set of experiments, the activity of these nickel catalysts was evaluated at atmospheric pressure and 873 K. Figure 6 presents the product composition of the glycerol steam reforming over the different nickel based catalysts. For all catalysts, glycerine conversion was 100 % and hydrogen was the major component in the gas phase. The use of Ce, La, Mg and Zr as promoters of Ni based catalysts increases the hydrogen selectivity compared to the reference catalyst supported on bare alumina. It can be seen that the Ni/AZ sample was the most selective catalyst with a gas composition after steam reforming similar to the values predicted by equilibrium. On the contrary, the catalyst supported on bare alumina showed the lower hydrogen selectivity among the tested samples. Differences in activity were explained in terms of enhancement in: surface nickel concentration (Mg), capacity to activate steam (Zr) and stability of nickel phases under reaction conditions (Ce and La).

Recently, Hirai et al [68] have reported the performance of noble metal based catalyst for glycerol reforming. A range of catalysts were test. The catalysts loaded with Group 8-10 metals were prepared using  $Y_2O_3$ ,  $ZrO_2$ ,  $CeO_2$ ,  $La_2 O_3$ ,  $SiO_2$ ,  $MgO$ , and  $Al_2O_3$  as supports. The reforming reaction was conducted with an aqueous solution of glycerin (special grade, from Wako Chemicals) at a temperature of 500-600 °C, atmospheric pressure, a steam-to-carbon molar ratio of  $S/C_1 = 3.3$ , and a W/F (contact time) of glycerin of 13.4 g-cat h/mol. Differences in the selectivity of the gaseous products were small among all catalysts. The order of the activity was as follows:  $Ru = Rh > Ni > Ir > Co > Pt > Pd > Fe$ . Among the catalysts studied thus far, ruthenium over  $Y_2O_3$ -supported catalysts exhibited highest glycerin conversion and  $H_2$  yield. However, ruthenium on basic  $MgO$  showed very low conversion of glycerin, compared to  $Y_2O_3$ - and  $ZrO_2$ -supported catalysts. Although  $Al_2O_3$  is used as a favorable support for the steam reforming of hydrocarbons, ruthenium on  $Al_2O_3$  showed the lowest conversion in the steam reforming of glycerin. Higher selectivity to  $CH_4$  and low selectivity to  $CO_2$  are reasons for the low  $H_2$  yield. All the catalysts showed high  $CO_2$  selectivity. These results can be explained by the high steam/carbon molar ratio under the reaction conditions used and the use of basic support materials, causing a promotion of the water-gas shift reaction.

Simonetti et al. [67] report results of catalyst characterization measurements for the conversion of glycerol to synthesis gas over various Pt-based catalysts. Carbon-supported Pt and Re catalysts were prepared by incipient wetness impregnation of carbon black (Vulcan XC-72) with aqueous solutions of  $H_2PtCl_6 \cdot 6H_2O$  and  $HReO_4$  (StremChemicals). Reaction kinetics



measurements at 498– 548 K for the conversion of glycerol to synthesis gas in the vapor phase over Pt/C and Pt–Re/C catalysts showed that stable catalyst performance could be achieved at low conversions.

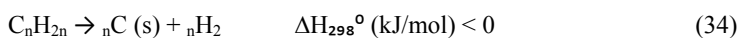
Steam reforming of glycerol was also examined over these  $M/\text{CeO}_2$  catalysts where M is Ir, Ni and Co. by Zhang et al. [69]. The Ir/CeO<sub>2</sub> catalyst showed the highest catalytic activity, and the complete conversion of glycerol was achieved at 400 °C with hydrogen selectivity of 85%. While the complete conversions of glycerol over the Co/CeO<sub>2</sub> and Ni/CeO<sub>2</sub> catalysts were obtained at 425 °C and 450 °C with hydrogen selectivities of 88% and 75%, respectively.

### 8.1.2. Coke Formation

Carbon deposition on the surface of the catalyst will result several undesirable reactions and products affecting the purity of the reformation products. Formation of carbon will cause loss of effective surface area, lower the heat transfer rate from catalyst to gas, and plug of the void space.

At 1000K no carbon is formed at any WGFR. At WGFRs 6:1 and 9:1, carbon formation is thermodynamically inhibited at any temperature. While increasing WGFRs from 1:1 to 3:1, carbon formation drops significantly [70].

As discussed earlier, the coke formation is not desirable in the steam reforming process. Compared to methane, glycerol exhibits a greater tendency to form carbonaceous formation. At high temperature (> 920 K) steam cracking may occur to form alkenes which may be easily form carbon through reaction (34), which is irreversible:

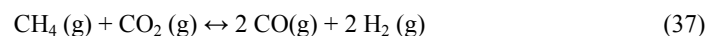
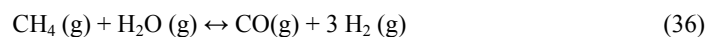
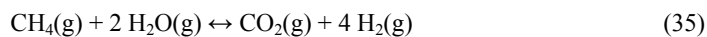


### 8.1.3. Temperature and Pressure

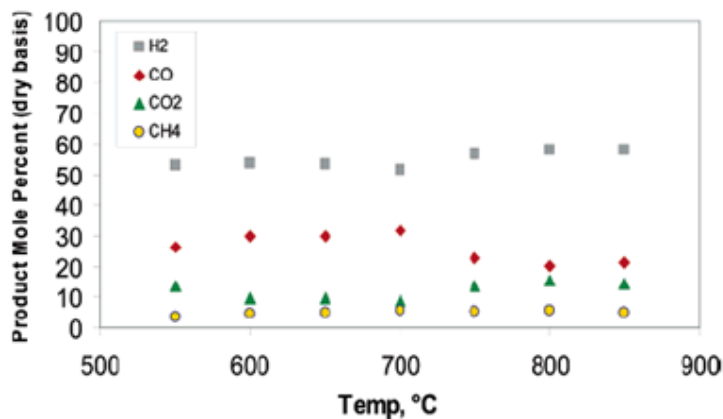
As can be observed in steam reforming of ethanol, the number of moles of hydrogen increases with increasing the temperature. The number of moles of hydrogen is at its maximum at 960K and decreases thereafter. A similar observation was made by Semelsberger and Borup [74] in dimethyl ether steam reforming. Moles of hydrogen decrease together with CO<sub>2</sub> at temperatures higher than 960 K, and at the same time, moles of CO and water increase. Perhaps, this can be explained by the reversible character of the WGS (eq.18).



As the temperature increases, moles of water and CH<sub>4</sub> decrease with increasing CO, CO<sub>2</sub>, and H<sub>2</sub>. This can be attributed to the methane steam reaction to produce CO or CO<sub>2</sub> and H<sub>2</sub> as given by the following equations (eqs 35,36). This behavior also may be attributed to the reformation of CH<sub>4</sub> with CO<sub>2</sub> (eq 37).



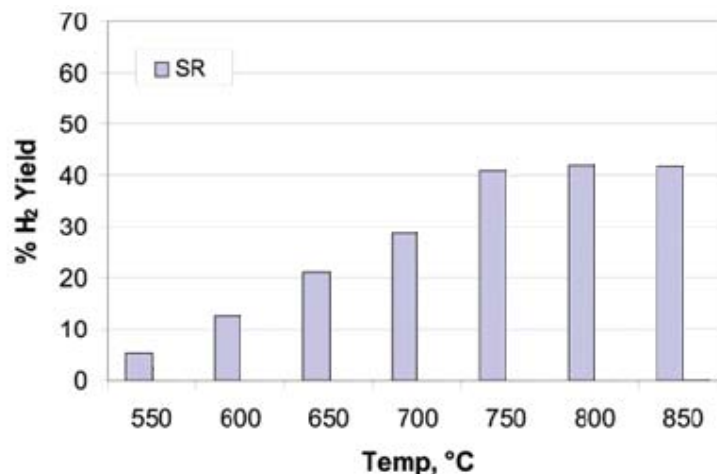
Swami, S. and Abraham, M. [29] also proved the influence of the temperature in the process. Figure 7 provides the percentage composition (mole percent on a dry basis) of the gas products as a function of reaction temperature during steam reforming of glycerol. The results indicate that the gas contained between 50 and 60% hydrogen, with slightly higher hydrogen concentrations at higher temperatures. CO is the dominant carbon product, particularly at lower temperatures. At temperatures of 700 °C and above, CO<sub>2</sub> and CO compositions are roughly equivalent. Some methane is also produced in low concentration (<10%) at all temperatures.



Source: [29]

**Figure 7: Product gas composition (dry basis) obtained during steam reforming of glycerol (S/C = 3) over Pd/Ni/K catalyst as a function of reaction temperature.**

Figure 8 compares the hydrogen yield as a function of temperature for steam reforming. The hydrogen yield increased with temperature.



Source: [29]

**Figure 8: H<sub>2</sub> yield obtained during steam reforming (S/C = 3) of glycerol over a Pd/Ni/Cu/K catalyst, as a function of reaction temperature.**

In contrast with temperature, the number of moles of hydrogen increases with decreasing pressure. The effect of the pressure on the glycerol steam reforming process is found to be consistent with ethanol steam reforming process [41]. However, higher pressure favors the formation of CH<sub>4</sub>.

#### 8.1.4. Water/Glycerol feed ratio (WGFR)

Similarly, the number of moles of hydrogen increases with the increasing WGFRs as happens with temperature. The molar fraction of hydrogen is found to be higher in case of low WGFRs. This is mainly due to the significant amount of water present in the product at high WGFRs [70]. The unreacted water reduces the molar fraction of hydrogen but not necessarily the quantity. The greatest quantity of hydrogen is produced at excess water at all temperatures. The best conditions to produce hydrogen will be with excess water if the purification problems can be overcome.

CH<sub>4</sub> production decreases when the WGFR increase. Molar fraction of CH<sub>4</sub> also decreases with the increase in WGFR. However, at WGFR 1:1 the CH<sub>4</sub> formation is lower compared to other feed ratios analyzed in the study. This can be due to the significant amount of carbon formation. Although, CH<sub>4</sub> formation is low at low WGFR, the molar fraction is higher than other feed ratios.



## 9. ENGINEERING POINT OF VIEW

### 9.1. Hot sources

A hot source is needed to sustain the reaction occurring in the steam reforming (SR). The hot source used is a process stream at high temperature (an internal source of heat). When this source of heat is not at a proper thermal level, a portion of a stream can be combusted in a burner in order to obtain a hot exhaust gas. The burner can be fed by: (a) fuel (ethanol,  $\text{CH}_4$ , diesel,...), (b) synthesis gas or (c) hydrogen-rich stream. Two new variables shall be considered: the air/fuel ratio and the process stream not burned. The efficiency of the system decreases when the burned fraction increases. It must be noted that when an internal source is employed, it shall not be considered as heat exchanged. The energy recovered from exothermic stages (water gas shift and preferential oxidation) is normally used to improve the global efficient of the process to close the energy balance.

### 9.2. Temperature approach in the heat exchangers

In order to reduce the heat exchangers size, temperature differences must be as high as possible. This is a relevant question if the purpose is to reduce the volume of the entire device. However, the higher the temperature approach is, the lower the heat recovery will be. Thus, there is also a trade-off between system size and efficiency.

### 9.3. Air/fuel ratio in the burner

An adequate air/fuel ratio must produce a stream with enough heat content with a proper thermal level to keep temperature constant in the SR. A low ratio implies deficient combustion and a high ratio leads to a lower thermal level.

### 9.4. Process stream fraction not burned

In order to minimize the burned process stream fraction, it would be necessary to choose the more adequate stream: fuel, synthesis gas or hydrogen-rich stream. It is not the aim of this work to discuss which stream is the most convenient.

### 9.5. Dimension

The lower space velocity than that used in reforming is the first drawback of this conversion process. While the reforming reactors usually work around 100.000  $\text{h}^{-1}$ , the high temperature water gas shift reactors (WGS-HT) usually work at 6000  $\text{h}^{-1}$  and the low temperature ones (WGS-LT) at 3000  $\text{h}^{-1}$  [61]. This causes the



design volume of the fuel processor to be greatly influenced by the water gas shift reactors size.

### **9.6. Spatial time**

The residence time increment (catalyst weight/vol. flow) guarantees the contact between reactants and catalyst causing the decrease in the molar flow of fuel feed into the reactor and the increment in the hydrogen yield.

### **9.7. Effect of tube diameter**

The internal distribution of the catalyst is favored by the increment in the tube diameter; it allows the work under permissible conditions of pressure drop and facilitates the heat exchange area to meet the heat requirements of the process. hydrogen yield suffers a fall with the pressure and is favored with temperature increase; because of these: the increase in the tube diameter could infer a decrease in the hydrogen yield due to the total pressure effects (small reductions), however, this fall is compensated with the increment of the heat transfer area which is a key parameter to supply the process energy requirements to complete the reforming reactions (methane reforming).



## 10. CONCLUSIONS AND RECOMMENDATIONS

The global and equilibrium analyses, both show a decrease in thermal efficiency for reforming larger hydrocarbons compared to methane. Hydrogen and electricity seem to be the key solutions for the 21st century, enabling clean efficient production of power and heat from a range of primary energy sources. Today, hydrogen is mainly produced from natural gas via steam methane reforming, a process suffering from several limitations, like the thermodynamic equilibrium limitations, high energy demand, catalyst deactivation due to carbon deposition and increased CO<sub>2</sub> emissions.

From the process engineering point of view, the following issues need to be addressed: reforming should preferably be carried out at low temperatures and atmospheric pressures to reduce the operating costs; the catalyst should provide high selectivity to H<sub>2</sub> and inhibit CO and by-products formation such as methane; the catalyst must resist coke formation which reduces the number of active sites and hence the reaction rates and implies regeneration process which are costly.

Feedstock issues, such as supply, cost, logistics and the value of coproducts, are major factors in cost-effectiveness of the hydrogen production process. Work is in progress to develop decision models for selecting among feedstock, process, and deployment alternatives.

Moreover, a reexamination of petroleum-fueled internal combustion engine (ICE) vehicles as the basis for road transportation throughout the world is being pursued on the grounds of (i) the increasing concern about the environmental consequences of fossil fuels used for vehicles propulsion; (ii) the global earth warming; (iii) the growing dependence of the industrialized countries on fossil oils; and (iv) the increasing global awareness of how human activities influence the environment and how a sustainable development can be achieved with the increasing world population. Although modern cars emit far less toxic pollutants including hydrocarbons, nitrogen oxides, carbon monoxide, and particulates, their increasing number is resulting in increasing automobile pollution. This brought about always further and further restrictive emission legislations all over the world, in line with the Kyoto Protocol, which paves the way to the introduction of zero-emission vehicles (ZEVs). This results in ever-increasing attention on the hydrogen utilization as energy vector.



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