

# **SAFETY ASPECTS IN THE PRODUCTION AND SEPARATION OF HYDROGEN FROM BIOMASS**

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Tecnalia is working in the development of gasification technology for the production of hydrogen from biomass. Biomass is an abundant and disperse renewable energy source that can be important for the production of hydrogen. The development of hydrogen system from biomass requires multifaceted studies on hydrogen production systems, hydrogen separation methods and hydrogen safety aspects. Steam gasification of biomass produces a syngas with high hydrogen content, but this syngas requires a post-treatment to clean and to separate the hydrogen. As a result of this analysis, Tecnalia has defined a global process for the production, cleaning, enrichment and separation of hydrogen from the syngas produced from biomass gasification. But, besides the technical aspects, safety considerations affecting all the described processes have been identified. For that reason, it is being developed a procedure to establish the technical requirements and the recommended practices to ensure the highest level of safety in the production and handing of hydrogen.

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## **1. Introduction**

During the last decade, the interest in the use of biomass for power generation has increased due to the environmental benefits that entails. Biomass is a renewable source of energy that generates low emissions of SO<sub>2</sub> and CO<sub>2</sub>, contributing positively to mitigate the greenhouse effect.

Currently 14% of total world energy consumption is covered by biomass. However, there is much more potential to produce at least 50% of Europe's energy requirements.

Technologies for primary conversion of biomass for electricity production are combustion, gasification and pyrolysis. Gasification combined with a gas engine has the advantage of generating greater electrical efficiency and reduced cost of electricity compared to combustion. Fluidized bed gasifiers provide excellent gas-solid contact, generating high levels of conversion. It is also possible to add catalyst to the bed to facilitate the cracking of hydrocarbons generated in the reaction and, therefore, reduce the tar content in the flue gas. The conversion of biomass into a hydrogen-rich gas is considered a future competitive method to produce energy and chemicals from renewable sources. The technology used for this purpose consists of a gasification system with steam feeding. But, besides the technical aspects, also safety considerations affecting all the process have been identified. For that reason, it is developing a

procedure to establish the technical requirements and the recommended practices to ensure the highest level of safety in the production and handing of hydrogen. The mentioned process is being studied at pilot plant scale. There are yet no full scale plants.

## 2. The process to obtain hydrogen from biomass

The gasification technology is a clean and efficient energy process that transforms biomass into a useful resource for further energy application. Gasification is the conversion of an organic material into combustible gas, through its reaction with a gasification agent (air, oxygen and water) in substoichiometric conditions. The gaseous products obtained are mainly H<sub>2</sub>, CO, CO<sub>2</sub> and methane. The total combustible gaseous products can be used directly in the same equipment and facilities that use natural gas or petroleum, which is a big advantage from the economic point of view. The heat required for the gasification reactions is obtained by partial combustion of char originated during the process, so the process can be thermally self-sustaining. The gasification is carried out at temperatures of 850-950° C, and the quantity, composition and calorific value of gas produced, or syngas, depends largely on the gasification agent and the material used in the reaction.

Gasification agents generally used for biomass gasification are air, oxygen and steam. When air is used as gasification agent, the gas obtained is poor with a low calorific value between 900 and 1,600 kcal/Nm<sup>3</sup> susceptible of being used in a combustion engine. If the gasification agent used is oxygen, it produces a gas with a low calorific value between 2.200 - 4.500 kcal/Nm<sup>3</sup> that can be used for energy recovery and for the synthesis of organic compounds (such as methanol). Another option is to use steam as gasification agent, allowing a greater proportion of H<sub>2</sub> in the synthesis gas generated (60%).

Table 1: Synthesis gas composition according to gasification agent.

Gasification agent	Low Calorific Value (Kcal/m <sup>3</sup> )	Gas Composition (% vol) Dry based				
		H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub>
Air	< 1.500	15	15	18	2	50
Steam	3.000-7.000	52	20	22	6	--
Oxygen	3.000-7.000	32	48	15	2	3

Gasification technology is considered a promising and attractive alternative to obtain hydrogen from biomass due to the environmental benefits like:

- reduction of emissions due to its renewable aspect
- good scenario for joint use in Fischer-Tropsch synthesis

As table 1, the better gasification agent for the production of hydrogen from biomass is steam. With the utilisation of steam is possible to obtain a syngas with 40-50%Vol dry based of hydrogen, coming mainly from the decomposition of water present.

The steam gasification is a highly endothermic process, so it requires a large amount of heat to be carried out. This heat can be managed through the partial oxidation of the biomass, through an oxygen supply with the gasification agent, or from outside, through the reactor walls. The supply of oxygen with the steam makes the process more feasible to get the reaction temperature required.

An efficient way to increase the hydrogen content of synthesis gas is through the use of catalytic beds, either in the gasification bed or in a bed after the gasification reactor. Through the catalytic reactions the tars contain the synthesis gas can break, to H<sub>2</sub> and CO. With the introduction of several reactors, after the gasification process, is possible to increase the hydrogen content in the synthesis gas. The first reactor used is a catalytic cracking feeded with steam for the reaction of the tars present in the synthesis gas. Next, enter a steam methane reformer, which generate CO and H<sub>2</sub>. Finally, the CO is converted to H<sub>2</sub> and CO<sub>2</sub> by reaction with water vapour through the CO-shift reaction. The hydrogen-enrichment methods are costly because of its energy requirements. Furthermore, these methods do not generate pure hydrogen gas, so it is necessary a final separation stage (by membrane, PSA, etc.).

The basic outline of the process to obtain hydrogen from biomass via gasification technology is:

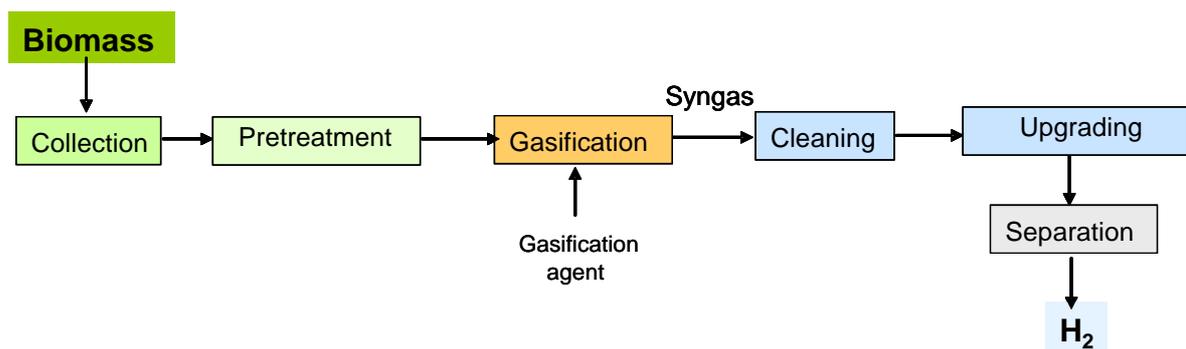


Figure 1: Chain of H<sub>2</sub> production via biomass gasification.

The steps to produce hydrogen from biomass via gasification are:

1. Biomass pre-treatment. Before the biomass is introduced into the gasification reactor, it must be conditioned to maximize the process efficiency. This pre-treatment includes the reduction of the particle size and the drying of biomass to a value of approximately 15% moisture.
2. Gasification. Once the biomass is in the adequate size and moisture, it is introduced into the gasification reactor continuously. To obtain a high concentration of hydrogen, it is used steam as gasification agent, being the reaction temperature of 850° C.
3. Gas cleaning. After the gasification process, it is necessary a gas cleaning unit to remove ash and tars from the system. This is accomplished with a system of scrubbers and cyclones.

4. Hydrogen upgrading. The clean synthesis gas is introduced into a steam reformer. With this process, the methane reacts with steam to generate CO and hydrogen. It is a catalytic process (Ni/Al<sub>2</sub>O<sub>3</sub>) conducted at 900°C and 20 bar. Then, the gas undergoes the shift reaction. Here, the CO reacts with steam to produce CO<sub>2</sub> and hydrogen. It is a catalytic process that requires concentration of tars max 2g/Nm<sup>3</sup>, otherwise catalyst deactivation is very fast.

5. Hydrogen separation. To obtain hydrogen it is necessary the removal of CO<sub>2</sub>. It is possible by physical methods; one of the most common is the Pressure Swing Adsorption (PSA), or the use of hydrogen permeable membranes.

Figure 2 shows the different concentrations of hydrogen along the various stages of the process.

In all these processes, there is an action with hydrogen, so a procedure for any eventually incident has to be implemented. To ensure the proper operation of the process, it has developed a procedure based on ISO/TR-15916, *Basic considerations for the safety of hydrogen systems*.

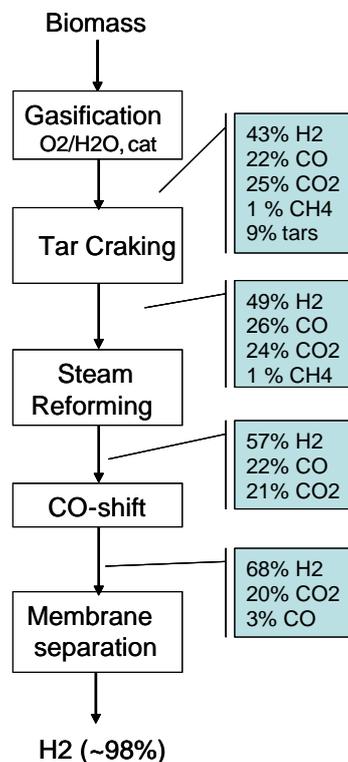


Figure 2: Hydrogen concentration along the process.

The major safety issue to be considered in all the process is the exhaust emissions possibility. There are very limited detailed data on the exhaust gas composition. It is an essential prerequisite for the complete risk assessment process to first analyse the hazards and then go on to assess the risks that they present and determine what, if any, ameliorating measures should be taken.

### 3. Safety aspects of the process

Table 2 shows some properties of hydrogen. Gaseous hydrogen has neither a characteristic colour nor odour. It forms the smallest, lightest molecule of any gas. As a result, gaseous hydrogen better permeates through materials, passes through smaller leak paths, diffuses more rapidly in surrounding media, and has greater buoyancy than other gases. The consequences, arising from these properties, are that released hydrogen rapidly rises and diffuses, but if confined, it can accumulate in high spots.

Hydrogen vessels and piping systems require good seals, and leaks are always a concern. Furthermore, hydrogen leaks are difficult to detect without help senses, if they do not make an audible noise. It has been demonstrated that hydrogen can permeate slowly through confined materials. The permeation rate varies for different kinds of materials. For metals such as steel, at ambient temperature, the rate is extremely low with insignificant quantities permeating over very long periods of time. Some caution should be observed with polymeric materials, which allow greater permeation and thus significant quantities of hydrogen can accumulate, if the flow enters into a small unventilated volume. Hydrogen gas dissolved in a liquid can permeate into adjoining vessel materials.

Table 2: Some hydrogen properties.

H <sub>2</sub> Flammability limits, vol fraction %	4,0 to 75 (in NTP air) and 4,1 to 94 (in NTP oxygen)
H <sub>2</sub> Detonability limits, vol fraction, %	18,3 to 59 (in NTP air) and 15 to 90 (in NTP oxygen)
Ignition energy (minimum) for ignition in air	0,017 mJ
Auto-ignition temperature,	858K
Flame temperature in air,	2318K

The principle hazard presented by the gasification and posterior separation process described for hydrogen production is the uncontrolled combustion of accidentally released hydrogen. This holds true because of the high potential for leaks and formation of combustible mixtures, the ease of ignition of these mixtures, and the potential for high-energy releases that can occur as a fire or an explosion.

For hydrogen to combust, two additional elements need to be present: an oxidizer such as air and a source of ignition. Mixtures of hydrogen and oxidizers are flammable over a wide range of concentrations, pressures and temperatures. Mixtures are readily ignitable near stoichiometry. Because of the ease of ignition of hydrogen/oxidizer mixtures, most methods for the reduction in risk of hydrogen combustion rely on separation of hydrogen from the oxidizers.

Gas explosion at biomass gasification facilities can occur when a mixture of combustible gases (mostly CO, H<sub>2</sub> and higher hydrocarbons) and oxygen within the flammability limits meets an ignition source. A gasifier plant routinely passes through the Lower Explosive Limit (LEL) and Upper Explosive Limit (UEL). The limiting oxygen concentration depends on the producer gas composition, the moisture, the temperature and the pressure. For hydrogen and carbon monoxide at room temperature

and ambient pressure, the limiting oxygen concentration is about 4%. In particular, a dangerous situation may occur during plant start-up, at shutdown and in an emergency case of uncontrolled air intake, for instance due to leakages. Also Specific attention should be paid with:

- Hybrid mixtures, where there is a combination of a flammable gas and dust.
- Ignition sources, that can be sparks resulting from the build-up of static electricity, glowing particles (char, partially converted biomass), lightning electrical or mechanical sparks (from an electromotor of the blower for instance), hot work (welding, cutting, grinding and sawing), hot surfaces, self-ignition in dust layers and open flames.
- Product gas from gasification, that can auto-ignite at temperatures above 600-650°C. If a small amount of air is added to gas at high temperature - or vice versa – a quiet combustion will take place at the air/gas interface. If gas and air can be mixed without immediate reaction and subsequently set on fire by an external source such as a spark or a glowing particle, gas explosion may take place, the reaction velocity and the peak pressure depending on the degrees of turbulence and confinement of the gas mixture

Safety considerations that arise from the gaseous hydrogen deflagration and detonation behaviour include understanding:

- whether system failures can lead to hydrogen-oxidizer mixtures,
- the influence of confinement both within and outside of the system, and
- the consequences of formation of high pressures, high temperatures and rapid propagation of flame fronts.

The conditions necessary for liquid-phase detonation are not typically found in the gasification equipment. Deflagrations of gaseous hydrogen-air mixtures can produce pressures as much as 8 times the initial pressure. Detonation of hydrogen-air mixtures can produce pressures as much as 16 times the initial pressure and with reflection, pressures 50 times the initial pressure. One important consideration is that the relief systems, designed to protect hydrogen systems from overpressure, rely on sensing the build-up of pressure.

As the gasification process used to produce hydrogen from biomass is feeded with steam, the presence of air is very limited, so the process is safer compared with air gasification. But, however, the risk exists so safety measures should be taken.

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