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Renewable Hydrogen Production through the Purification of Syngas into Metal Hydrides in an Integrated Electrolysis and Biomass Gasification Plant

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Abstract. Hydrogen produced from renewable sources will play a pivotal role in the transition to a decarbonized economy, in particular in the transportation and industrial sector. However, this pathway faces several challenges in terms of cost, efficiency, lifetime, etc.
Several technologies can be used to produced renewable hydrogen. Among them, water electrolysis and biomass gasification offer a high level of maturity, and their integration can improve the availability of hydrogen from renewable sources, reducing the impact of fluctuating sources, such as solar or wind, while offering the possibility of supplying not only hydrogen, but also other valuable products for biofuel production. This integration requires the implementation of suitable purification methods to extract the hydrogen from the syngas produced in the gasification process.
This work presents an experimental purification facility for syngas using metal hydrides based on a FeTi alloy. The evaluation of this facility will analyse, after successive loading and unloading cycles, the purity of the gas obtained, the CO_2 and CO absorption capacity of the hydrides, the lifetime of this system in terms of number of cycles, the regeneration capacity, the total energy efficiency of the process, etc. Preliminary results of this evaluation will be presented at the congress.

Key words. Hydrogen production, biomass gasification, water electrolysis, hydrogen purification, metal hydride
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1. Introduction

Hydrogen produced from renewable sources will play a fundamental role in decarbonizing different economic sectors in which the direct use of electrical energy from renewable sources cannot fully satisfy users' needs, such as the transport sector, in which hydrogen-based electric vehicles will coexist with battery-based vehicles, or industry, where renewable hydrogen can be used as a raw material or for thermal energy generation.

In this scenario, the generation of hydrogen from renewable electricity through water electrolysis has been identified as one of the priorities in national and international strategies and roadmaps, to advance the production of low-emission hydrogen in the context of the energy transition. In the case of the EU, its hydrogen roadmap prioritizes the production of renewable hydrogen, using mainly wind and solar energy. Moreover, the hydrogen strategy for a climate-neutral Europe addresses the pathway to turn clean hydrogen in a key component in the EU's strategy to the energy transition, net-zero, and sustainable development, installing at least 6 GW of renewable hydrogen electrolysers in the EU by 2024 and 40 GW of renewable hydrogen electrolysers by 2030. Despite Nordics and Iberia lead the supply of electrolytic hydrogen by 2030, given the current conditions, this target of deploying 6 GWel by 2024 will not be achieved, due mainly to technical challenges to scale up hydrogen production plants, regulatory constraints, access to funding, and the development of pan-European infrastructure

Different electrolysis technologies use renewable electricity to split water into hydrogen and oxygen. Despite their rapid progress, electrolyzers still face significant challenges in terms of cost, lifetime, and operability under varying conditions, such as those required for coupling to renewable sources. In addition, other processes allow renewable hydrogen production, with biomass gasification being one of the most technologically mature. Gasification is a thermochemical process that transforms biomass into gaseous fuels through a series of partial oxidation and reduction reactions that take place at high temperatures. These processes can occur with or without a catalyst. Biomass is converted into a synthesis gas or syngas, which is a mixture of CO_2, CO, H_2, CH_4 and other hydrocarbons, as well as N_2, if air is used as the gasification agent.
The result of the process is not only synthesis gas, but also other combustible gases, inert components, tar, charcoal, dust and other impurities. The energy inherent in the biomass is not immediately released during this process but is converted into the binding energy of lighter fuels rather than into the heat of the combustion products.

Biomass gasification can offer great operational flexibility to produce gases of different qualities for different applications, such as the production of liquid biofuels via the Fischer-Tropsch process, direct combustion, heat generation, boilers, electric power generation by motors and hydrogen production for different applications (e.g. power generation in fuel cells or feedstock in industrial applications). Depending on the oxidant used, the process can be classified as (i) air gasification, (ii) oxygen gasification and (iii) steam gasification [48]. The composition of the syngas depends mainly on the composition of the biomass and the operating conditions of the gasifier. The efficiency of the gasification process is influenced by factors such as biomass composition, process temperature and the presence of catalysts. The potential of different gasification methods to produce H_2 should be highlighted to demonstrate the abundance, relatively low cost and wide applicability in a variety of sectors for biomass conversion. For example, a H_2 production cost in the range $1.77-2.05/kg has been estimated for a plant with a planned H_2 production of 139,700 kg/day and a biomass cost of $46-80/dry tonne [1,2].

To achieve these targets, high-efficiency and low-cost hydrogen recovery and purification technologies from the hydrogen gas mixtures are crucial for the development of hydrogen-related industries and hydrogen energy applications [7,8]. For example, regarding the use of hydrogen from biomass in fuel cell vehicles, it should fulfil the SAE J2719:2020 and ISO 14687: 2025 standards. In this case, the minimum mole fraction for the fuel is 0.9997, with a maximum allowed content of carbon dioxide (CO_2) of 2 ppm, and 0.2 ppm of carbon monoxide (CO).

There are three main commercially available purification methods: pressure swing adsorption (PSA), membranes, and cryogenic distillation. PSA occupies a prominent place in the market for large-scale H_2 purification plants. Approximately 85% of H_2 produced from reforming of natural gas is purified using the pressure swing adsorption (PSA) process due to its high flexibility, efficiency, high product purity (>99.9%), and low energy consumption Pressure swing adsorption (PSA) technology has long been used in the industrial-scale petroleum refining process. [3]

On the other hand, cryogenic distillation is an energy-intensive process because it operates at extremely low temperatures. However, it provides low levels of purity that usually do not meet the criteria required for fuel cell vehicles. Finally, hydrogen purification membranes are commonly used at small and medium commercial scales, mainly due to the high cost of the required materials (e.g. palladium) [4].

In addition to these commercial technologies, metal hydrides (MH) can also be used to extract high purity hydrogen from gas mixtures due to their selective absorption capacity, high product purity, relatively good operating conditions and safety. Hydrogen storage in MH is based on a chemical process in which hydrogen reacts reversibly with a metal alloy to form MH through absorption and desorption processes. During the hydrogen absorption process, only hydrogen enters the metal hydride (MH) bulk, while other impurities (such as CO_2) remain in the gas phase. However, this absorption process can be affected by the effect of impurities in the MH, which has a significant impact on hydrogen recovery and purification. During the hydrogen desorption process, high purity hydrogen is obtained, assuming that potential impurities have little effect on the desorption process.

Impurities have varying effects on the performance of metal hydride devices. Depending on the alloy and impurity combination, the hydrogen storage properties can be degraded by different types of damage such as poisoning (H_2S), retardation and corrosion (water vapour, CO_2) and inert gas blanketing (N_2). Several fundamental investigations have been carried out to assess the interactions of impurity gases with metal hydrides. Some of these developments have been implemented on an industrial scale (e.g. hydrogen extraction from ammonia production). The feasibility of metal hydride applications for hydrogen extraction from gas mixtures containing CO_2 has also been evaluated [5,6].

In the framework of the AIHRE project (Analysis and Promotion of Renewable Hydrogen in the Spain-Portugal Cross-Border Region), the Energy Laboratory of the National Institute of Aerospace Technology (INTA) is evaluating, from a technical and economic point of view, the hybridization of both technologies, to integrate both production processes and optimise the generation of different products, including high purity renewable hydrogen, suitable for use in vehicles or other fuel cell-based applications; mixtures of renewable CO_2 and hydrogen, suitable for the production of biofuels, and even biogenic CO_2 [8]. Figure 1 shows this concept.

The figure shows that the process integration considers the use of the oxygen produced in the electrolyser as a reducing agent in the gasification process and also considers the potential use of the heat generated in the electrolyzer stacks to increase the overall efficiency of the plant.

In this integration, the purification of syngas to obtain high-purity, fuel cell grade, hydrogen plays a fundamental role.

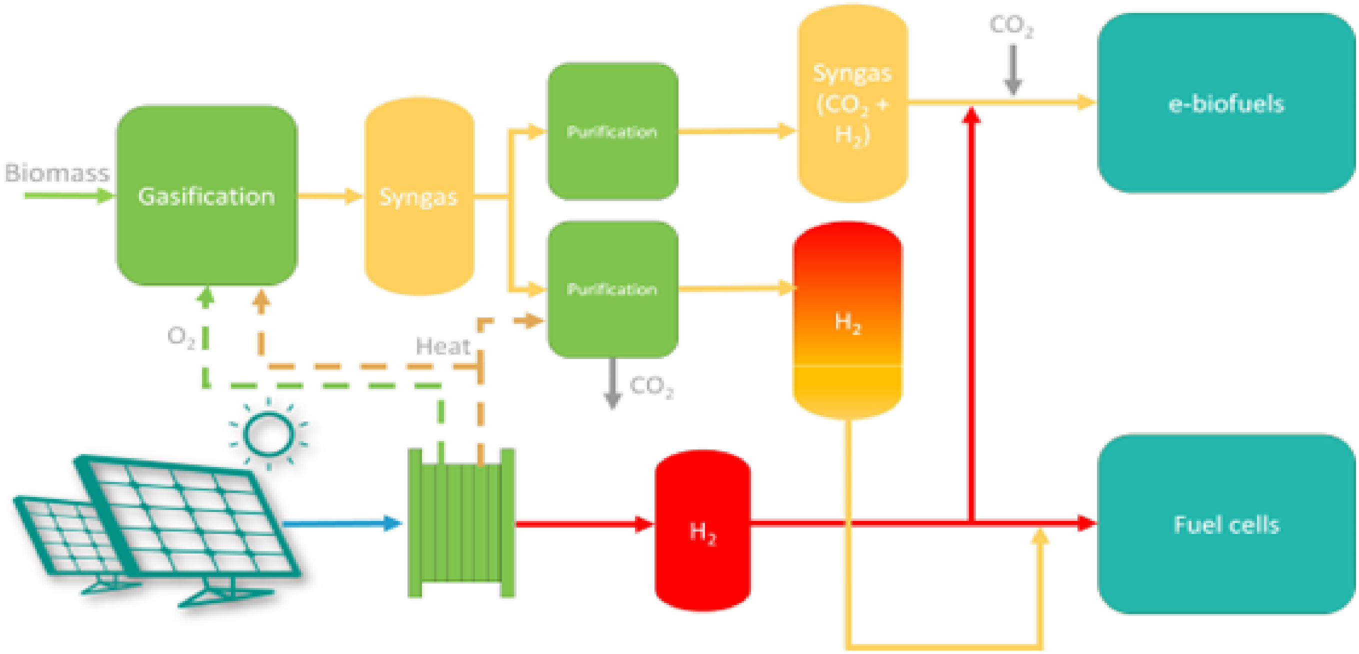

Fig. 1. Integration of electrolysis and biomass gasification concept in AIHRE project

2. Experimental facility and methodology

The AIHRE project has analysed the potential for hydrogen production and the composition of the synthesis gas from different types of biomass, such as olive or vine prunings, forestry waste, etc., using different gasification technologies.

The experimental unit developed at INTA includes a gas mixer designed and built to simulate the above synthesis gas compositions. The resulting mixture is stored and purified in a FeTi metal hydride tank. Figure 2 shows the diagram of this facility.

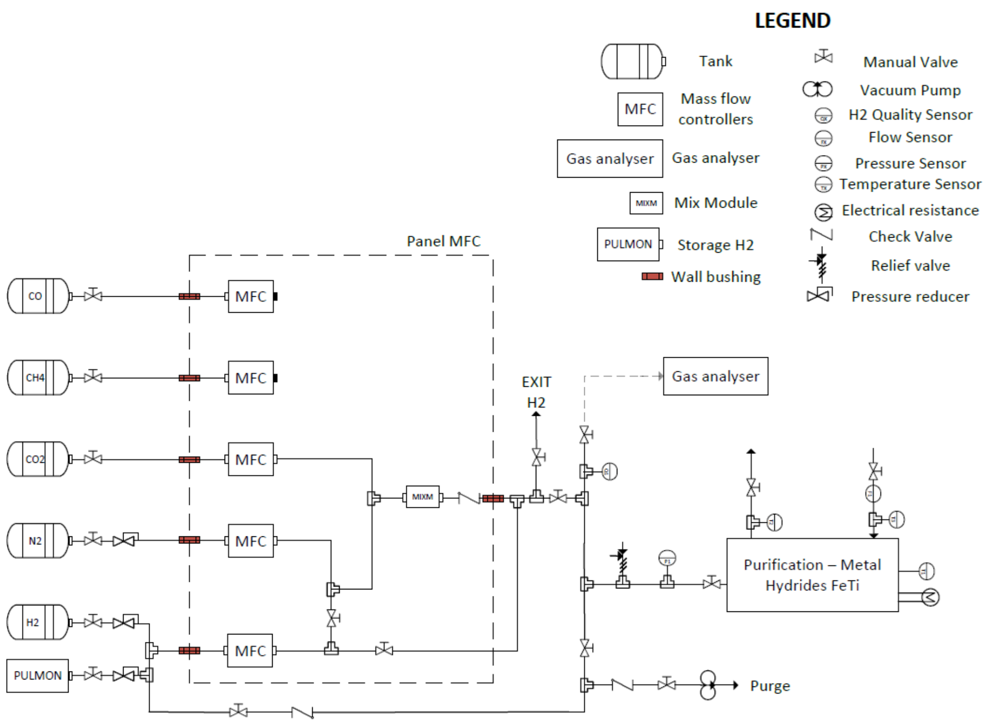

Fig 2. Gas mixer and MH purification system.

The main components of this experimental facility are:

- A supply of several gases (typically present in syngas composition) to simulate the different compositions to be analysed. Hydrogen and nitrogen, available on the laboratory's gas networks, will be used initially, while the remaining gases will be supplied from gas cylinders connected to the mixer via dedicated lines.
- Mass flow controllers (MFCs) are responsible for regulating the precise flow of each gas. They ensure that the input proportions remain stable and meet the required specifications.
- A mixer where the gases controlled by the MFCs come together to form the pre-determined mixture. This system is designed to ensure a homogeneous mixture of gases before they enter the hydride storage.
- The mixing module, a system that verifies that the gas mixture has been correctly mixed. This module compares the actual mixture proportions with the programmed proportions.
- A gas analyser and hydrogen quality sensor, which analyse the final composition of the gas mixture to determine the concentrations of each component. This step is crucial for validating process efficiency and optimising production.

The control and data acquisition system (SCADA) controls the entire emulator process and the hydrogen purification and storage system. This system provides an interface for real-time monitoring of critical variables, safety alerts, and operating settings. This data acquisition system basically consists of a series of sensors that provide information on various parameters, such as pressures, gas temperatures, cooling water temperatures, gas and cooling water flow rates, etc.

The project will experimentally evaluate the feasibility of using metal hydrides based on a FeTi alloy for this separation of hydrogen from the other gases in the mixture. This storage system consists of seven tubes containing the FeTi alloy, integrated in a shell that allows the circulation of cooling water for evacuation, generated during the hydrogen charging process, as well as the thermal energy that must be supplied during the discharge process. The whole system has a maximum hydrogen storage capacity of 11 Nm^3. Figure 3 shows the metal hydride tank.

Fig 3. FeTi metal hydride tank.

The system will be tested with different gas mixture compositions in successive loading and unloading cycles to evaluate the purity of the gas obtained, the effect of CO_2, CO and other impurities on the hydrogen storage capacity of the hydrides, the lifetime of this system in terms of number of cycles, the regeneration capacity and the overall energy efficiency of the process.

Preliminary results of this evaluation will be presented at the congress.

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