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## Review Article

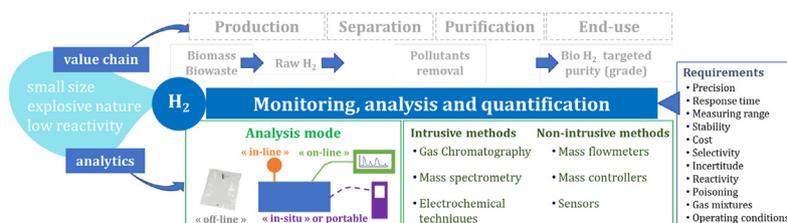
# Monitoring, analysis, and quantification of hydrogen from biomass and biowaste: A review

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Hydrogen is called to play a crucial role in decarbonizing different sectors by meaningfully reducing their emissions. Hydrogen production from biomass and biowaste has recently gained momentum due to the high availability of the resource and maturity of thermochemical conversion technologies. However, hydrogen monitoring and purification is required to optimize the process and to meet end-point-applications specifications. This paper provides a comprehensive state-of-the-art on the hydrogen monitoring, analysis, and quantification techniques, with a focus on gas mixtures containing hydrogen. Precision, response time, stability, selectivity of the methods together with other key parameters namely poisoning, interaction with other gases, hydrogen concentration, operating conditions, are confronted. The need for fast and precise hydrogen quantification, especially in the case of complex gaseous mixtures and for high-grade hydrogen applications, together with the need of reliable standards and materials able to provide fast hydrogen adsorption-desorption cycles are the main challenges that arise from our analysis.

**List of abbreviations**

AED	atomic emission detector	micro-TCD or $\mu$ TCD	miniaturized TCD
Bio-H <sub>2</sub>	Biohydrogen	MS	Mass Spectrometry
CCD	Catalytic Combustion Detection	MS-5A	Molecular Sieve columns type 5 A
CCS	CO <sub>2</sub> Capture and Storage	NL	normal litters
CFV	Critical Flow Venturi	NREL	National Renewable Energy Laboratory
ECD	Electron Capture Detection	OFCEAS	Optical Feedback Cavity Enhanced Absorption Spectroscopy
EI	Electron Ionization	PDD	Pulsed Discharge Detector
ESI	Electrospray Ionization	PDHID	Pulsed Discharge Helium Ionization Detector
FID	Flame Ionization Detector	PEMFC	Proton Exchange Membrane Fuel Cell
FTIR	Fourier Transform InfraRed spectroscopy	PIC	Photometric Ionization Detection
FTS	Fischer-Tropsch Synthesis	PLOT	Porous Layer Open Tubular
GC	Gas Chromatography	PM	Particulate Matters
GTR	Global Technical Regulation	PPQ	Porapak Q column
HID	Helium Ionization Detector	QMS	Quadrupole Mass Spectrometer
HSGC	High-Speed Gas Chromatography	SCD	Sulfur Chemiluminescence Detection
HyWAM	Hydrogen Wide Area Monitoring	SOFC	Solid Oxide Fuel Cells
ISO	International Organization for Standardization	sub-ppm	subparts per million
ITMS	Ion Trap Mass Spectrometer	TC	Thermal Conductimetry
LFL	Lower Flammability Limit	TCD	Thermal Conductivity Detector
<i>m/z</i>	mass-to-charge ratio	TDS	Thermal Desorption Spectrometry
MALDI	Matrix-Assisted Laser Desorption/Ionization	TID	Thermal Ionization Detection
MB-TDS	Molecular Beam-Thermal Desorption Spectrometry	TPD	Thermal Programmed Desorption
MEMS	Micro-Electro-Mechanic System	TPT	Thermal Programmed Techniques
micro-FID or $\mu$ FID	miniaturized FID	TRL	Technology Readiness Level
micro-GC or $\mu$ GC	Micro-Gas Chromatography	WGSR	Water-Gas Shift Reaction

## Context and challenges

The forecast through 2050 underlines a 50% increase in world energy consumption [1]. In parallel, the energy sector is the main source of greenhouse gas emissions. This raises interest in a complete transformation of the current energy system. The Net Zero by 2050 roadmap aims to reduce global CO<sub>2</sub> emissions through the deployment of the available clean and efficient energy technologies [2]. In such a scenario, hydrogen is projected as a fascinating energy carrier among the environmentally friendly solutions by using sustainable resources for its production. The hydrogen demand is expected to increase almost sixfold to reach 530 megatons of hydrogen by 2050, with half of this demand in industry and transport [3]. Tremendous efforts have been made in hydrogen production pathways, transport, storage, endpoint applications, and safety over the last decade. In this context, analytical techniques for hydrogen monitoring and quantification are crucial to optimize the effectiveness and ensure the reliability of the hydrogen production, purification, storage value chain.

## Hydrogen sources

As a versatile fuel, hydrogen can be produced from different energy sources through various technologies leading to different CO<sub>2</sub> footprints. Hydrogen produced from renewable sources is regarded as an alternative to black and grey

hydrogen obtained from coal and natural gas and has a high carbon footprint. Renewable hydrogen includes green hydrogen and bio-hydrogen, which were declined in different hydrogen colors depending on the origin of the resource leading to hydrogen production [4]. Green hydrogen is produced through electrolysis from wind, hydel, and solar energies. Bio-hydrogen is obtained by the thermochemical and biological transformation of biomass and biowaste (Fig. 1), through biological and thermochemical conversion routes [5].

Biological processes, such as digestion, fermentation, and esterification, produce hydrogen from biowaste using microorganisms with low energy consumption, with processes at low Technology Readiness Level, TRL (2–4). Hydrogen production can be carried out in continuous or batch mode. Photo-fermentation, water photolysis, and dark fermentation lead to direct hydrogen production from biomass by the action of microorganisms. Indirect production consists of producing intermediate compounds, such as ethanol, biodiesel, and biogas, which are then reformed into hydrogen [10,11]. However, the production rate of hydrogen in these direct processes is relatively low (from 2.5 to 25 mmolH<sub>2</sub>/l (reactor)/h [12]), which may be analytically challenging [13]. Hydrogen quantification may be impacted by the presence of other gases in the culture medium, such as nitrogen [14].

Hydrogen production from thermochemical processes can be mainly carried out using biomass and biowaste

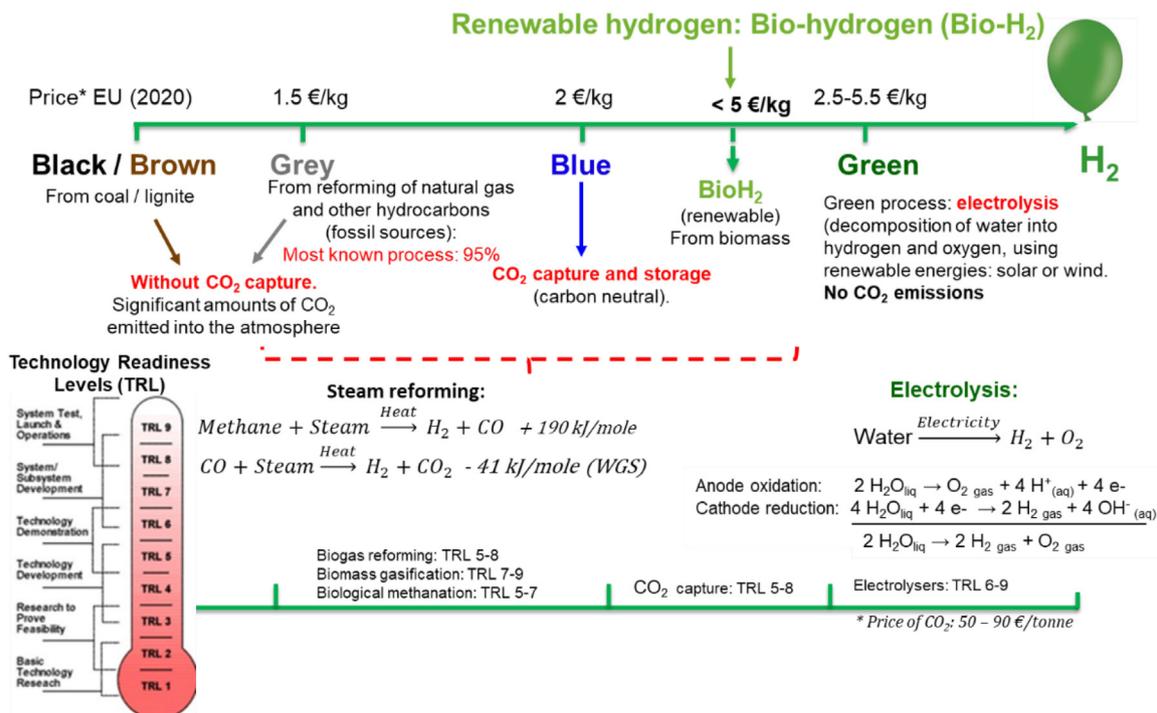


Fig. 1 – Technico-economic and hydrogen sources summary [6–9].

pyrogasification and biogas reforming. Pyrogasification typically runs from around 700 °C to 1200 °C, under steam or CO<sub>2</sub> atmosphere [15]. Biogas is obtained from the fermentation of biodegradable resources thanks to microorganisms. It is mainly composed of 50–65 vol% of methane (CH<sub>4</sub>), 30–40% of CO<sub>2</sub>, and 0–5% of O<sub>2</sub> [16,17]. Biogas reforming can be carried out under a dry (in presence of CO<sub>2</sub>), steam (H<sub>2</sub>O), or a partial oxidant atmosphere (O<sub>2</sub>), typically from around 800 to 1000 °C [17]. Both pyrogasification and biogas reforming produce syngas, which consists of a mixture of CO and H<sub>2</sub>, widely used in industry [18]. Furthermore, the water gas shift reaction allows the conversion of CO into CO<sub>2</sub> thanks to the presence of steam. Syngas composition is expressed by the ratio H<sub>2</sub>/CO, which is strongly dependent on the operating conditions and for which the interest varies as a function of the targeted application for syngas. For example, by increasing the CO<sub>2</sub> percentage in the gasification reactor from 0 to 50%, H<sub>2</sub>/CO ratio goes from 5.5 to 0.25 [19]. When targeting hydrogen valorization, the use of metallic catalysts during gasification will enhance tar conversion towards an increase in the H<sub>2</sub>/CO ratio [20]. Transition metal based-catalysts would also be required in the production of hydrogen from hydrothermal processes, such as supercritical water gasification [21]. Thermochemical conversion leads to high hydrogen production rates, at typically a high TRL for continuous processes, about TRL 6–7 for biogas reforming and TRL 8–9 for biowaste pyrogasification, while TRL for super-critical processes is still lower (Fig. 1).

While the production costs are much more competitive for hydrogen produced from coal and natural gas, their environmental impact in terms of CO<sub>2</sub> emissions is high, mostly when CO<sub>2</sub> sequestration is not proposed (Fig. 1). Green hydrogen production from biomass and biowaste reduces CO<sub>2</sub> emissions by introducing CO<sub>2</sub> into the carbon loop. This production route has gained momentum over the last few years, especially due to the maturity of the transformation technologies and the high availability of the resource at a local scale. The deployment at a larger scale (TRL >7), as well as the integration of hydrogen production in a biorefinery approach [5,22], will likely allow a much more affordable hydrogen price. It is forecasted to be around 5€/kg for hydrogen produced by thermochemical conversion of biomass with photosynthetic CO<sub>2</sub> generated, while the hydrogen from electrolysis will ring at 2€/kg without CO<sub>2</sub> emissions [3]. In terms of energy consumption, the energy required for hydrogen production from biomass gasification (78 KWh per Kg of H<sub>2</sub> [23]) was reported to be higher than for electrolysis (55 KWh per Kg of H<sub>2</sub>) and methane reforming (59 KWh per Kg of H<sub>2</sub>) [2].

Hydrogen pollutants are dependent on the feedstock composition [25]. The main hydrogen pollutants in pyrogasification include particulate matters (PM), gases, and condensable species [26]. This represents a main analytical challenge when handling complex gas/liquid mixtures that need to be separated and purified to achieve the targeted hydrogen purity for a given end-point application. The unprecedented potential of this production route, together with the associated analytical challenges, point out the need for a critical analysis of the existing techniques for hydrogen monitoring, analysis, and quantification, as well as an identification of the main analytical innovations that are expected

in the field in a near future. This review intends to fill this gap in providing insights on current trends in the field.

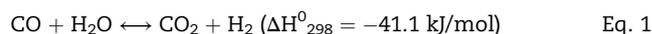
### Hydrogen purification

Whatever the application, hydrogen contaminants can cause negative reversible or irreversible effects [27]. The required level of purification of the produced hydrogen-rich gas varies significantly depending on the end-of-pipe applications associated with the given environmental regulations. For hydrogen fuel applications, the level of hydrogen purity requirements varies depending on the end-use technology [28]. ISO 14678:2019 suggested a classification based on three types of technical specifications for hydrogen fuel, including the purity grade and the tolerance to impurities according to the applications [28,29]. As for the transportation sector, the United Nations, through the Global Technical Regulation (GTR) on hydrogen and fuel cell vehicles, defined safety specifications on the hydrogen emissions ceiling for vehicles during their use and under accident conditions, as well as on the hydrogen emissions ceiling in normal operation [30].

Although the paper is focused on the analysis and quantification of hydrogen, the purification step before accurate analysis is an important step for a better understanding of the analysis that we propose. Hydrogen purification has been extensively developed in the last 30 years regardless of the resources and production technologies [25,31–37]. The selection of the optimum purification technique for each specific application is based on technical and economic criteria together with operational considerations such as hydrogen supply mode and source.

Carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>) are present in the raw hydrogen gas. Although they are most of the time considered as pollutants, they are platform molecules for many industrial applications. They may be separated or used as co-reactant with H<sub>2</sub> depending on the application requirements and process conditions. Thus, H<sub>2</sub>/CO ratio is the syngas key parameter for applications such as Fischer-Tropsch synthesis (FTS), gas turbines, and Solid Oxide Fuel Cells (SOFC) [31,32].

CO elimination through its conversion into hydrogen via water-gas shift reaction (WGS) (Eq. (1)) is considered the first step of hydrogen purification, which leads to a higher purity grade. The process can be carried out during the gasification process or downstream, in the presence of a catalyst.



CO<sub>2</sub> capture and storage (CCS) are considered a specific measure not only to reduce CO<sub>2</sub> emissions but also to supply CO<sub>2</sub> for several applications such as the production of chemicals (methanol), carbon nanotubes, and bio-composite foam plastics. A synthesis of the main technologies for CO<sub>2</sub> removal from gas streams was included in the Supplementary Material (S1). Principally, CO<sub>2</sub> can be removed from syngas through chemical and physical absorption, chemical looping, and hydrate-based separation.

Other main hydrogen pollutants are PM, H<sub>2</sub>S, HCl, NH<sub>3</sub>, and tar. The removal technologies comprise physical methods, such as filtration, and chemical methods, notably absorption

and adsorption. A synthesis of the main technologies for hydrogen purification targeting the removal of undesirable pollutants was included in the Supplementary Material (S2). It was shown that PM removal requires a heating step. H<sub>2</sub>S and HCl are removed by neutralization (acid-base reaction), while NH<sub>3</sub> is removed by absorption and oxidation.

The targeted level of purity depends on the end-point application and can be obtained via different separation and purification stages. The hydrogen concentration in the raw gas to be purified depends on the resource and the production process. After the separation of the main pollutants, the purification stage allows reaching the target hydrogen purity according to its application. Several market purification technologies can achieve high purity grades to fill the applications in mobility and fuel cells (Table 1). Nevertheless, the purification and separation steps in almost all large-scale manufacturing processes are often the most technologically challenging and economically limiting factors [38]. Indeed, the purification price varies with the hydrogen content in the feed and can even account for half of the hydrogen production cost. There are still challenges in scaling up some of the technologies to bring them to the marketplace.

As for the analysis and quantification of hydrogen, less has been published and discussed in the literature while this aspect is crucial for the development of hydrogen as an energy source. This explains the motivation for this contribution to the state-of-the-art in the field. While the literature provides already review on the production and purification of hydrogen from biomass and biowaste, the objective of this contribution is to synthesize and analyze available techniques and techniques under development for hydrogen monitoring, analysis, and quantification. It also targets the identification of the main analytical challenges and expected innovations, with a special focus on analytics related to complex gas mixtures of hydrogen produced from the thermochemical conversion of biomass and biowaste.

### **Analytical tools for H<sub>2</sub> detection, quantification, and monitoring**

The small size, explosive nature, and relatively low reactivity of the hydrogen molecule (H<sub>2</sub>) made its detection, quantification, and monitoring much more challenging than for other gases. The minimum ignition energy for hydrogen is an order of magnitude lower than that of hydrocarbons, corresponding to a lower flammability limit (LFL) of hydrogen of 4.0 vol% in air. Hydrogen detection is required from low concentrations, usually specified to either 10% LFL (0.4 vol%) or 25% LFL (1.0 vol%) [46]. Special attention needs to be paid to materials' permeability, to avoid hydrogen leaks or steel corrosion [47], as well as the risk of creating explosive environments when hydrogen is confined. Previous works in the literature studied and modeled hydrogen leaks in confined systems by using existing sensors [48,49], in some cases in combination with advanced data treatment methods [50].

In the literature, few studies are specifically devoted to the development of new analytical techniques for hydrogen detection and quantification. In most cases, standard techniques are used. In this section, we intend to discuss intrusive and non-intrusive measurement techniques for hydrogen

detection, quantification, and monitoring, both in terms of process implementation, scientific principles, main advantages, drawbacks, and challenges ahead.

#### *Analysis tools and procedures*

Detection and quantification techniques can be intrusive or non-intrusive. Measurements can be carried out off-line, after gas trapping or collection, or online, by using continuous and instantaneous detection methods or sensors. International standards define specifications for hydrogen detection apparatus, such as precision, response time, stability, measuring range, selectivity and poisoning (ISO 26142:2010 for stationary applications).

*Hydrogen sampling.* Sampling is the first step before carrying out offline measurements. It may be carried out by closed recipients with sorbent materials. When dealing with hydrogen, alone or in a gaseous mixture, explosion-proof materials with a very low permeability are required [15].

Gas collection in thermochemical conversion processes allows to estimate the total gas production and close the mass balance of the process. The gaseous mixture stability needs to be ensured during sampling and storage, by the absence of transformations such as evaporation, adsorption, degradation and oxidation.

Sampling without pre-concentration is possible in bags, canisters and gas collection tubes. This sampling method is suitable for permanent gases (H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> ...) as they may be stored at room temperature without condensation.

Cryogenic traps, which may contain a solvent, are used for condensable species retention [51]. However, their application to permanent gases, such as hydrogen, is more limited. In all cases, the length of the sampling line must be minimized, and the materials need to be carefully selected.

Innovative techniques, such as intraparticle gas sampling, reveal the evolution of chemical species, including hydrogen, during biomass thermal decomposition. The evolved gas generated in pyrolysis reactions is analyzed thanks to a sampling probe introduced in the center of a particle and connected to a gas detection system, such as a micro-GC [52].

When the concentration of the analytes is low or in traces, a pre-concentration can be preconized together with sampling. Sampling with pre-concentration may be carried out by selectively adsorbing the targeted compounds in a liquid or solid phase packed in a tube.

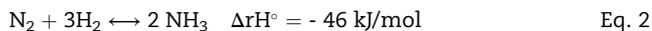
Materials developed for hydrogen storage are in principle suitable for hydrogen sampling [53]. However, the operating conditions required in some cases, such as very low temperature or high pressure, could be an issue with rapid hydrogen adsorption and desorption required for analysis. Hydrogen selective sorption is possible through solid storage materials with a variable degree of structural organization, such as carbonaceous materials, zeolites, and metal-organic frameworks (MOFs). The adsorption capacity of a material depends on the specific surface area, pore size, and surface chemistry. The duration and the flow rate of sampling need to be appropriate, so that targeted compounds can be entirely retained on the sorbent, in a sufficient quantity to enable their quantification. Then, hydrogen needs to be desorbed by heat or by solvent liquid extraction [15]. Hydrogen storage in solid

**Table 1 – Comparison of different features and aspects of hydrogen purification methods [33,39–45].**

Type	Physical		Diffusion	
Technology	Pressure swing adsorption	Cryogenic separation	Polymer membrane	Palladium membrane
Principle	Separation under pressure according to the molecular characteristics and affinity for an adsorbent material	Stepwise condensation of gas feed at low temperatures	Gas molecules passage through the holes of permeable membranes according to a solution-diffusion mechanism	
Operation conditions	2–15 MPa	150–75 °C	2–20 MPa	<2 MPa
Pressure and Temperature	ambient temperature		0–100 °C	300–500 °C
Feed hydrogen (%)	50–90	50–90	70–95	>98
Purity (%)	99–99.999	99–99.999	99.5%	99.99–99.999
H <sub>2</sub> recovery rate (%)	69–99.99.6	69–99.99.6	<85	99
Scale	Large	Large	Small to large	Small to medium
Advantages	<ul style="list-style-type: none"> <li>• Low operation cost</li> <li>• Long service life</li> <li>• Fast process cycle</li> <li>• Large scale use</li> </ul>	<ul style="list-style-type: none"> <li>• No chemical reagents or additives are used</li> <li>• Capability o to produce liquid CO<sub>2</sub> ready</li> </ul>	<ul style="list-style-type: none"> <li>• Novel separation concept</li> <li>• High selectivity</li> <li>• Low energy consumption</li> <li>• Simple modular systems</li> <li>• No waste streams</li> <li>• Low manufacturing cost and industrially established</li> </ul>	<ul style="list-style-type: none"> <li>• Selectivity reduction by the presence of CO<sub>2</sub></li> </ul>
Disadvantages	<ul style="list-style-type: none"> <li>• Large floor area</li> <li>• Inflexibility</li> <li>• Low adaptability</li> <li>• Low selectivity</li> <li>• Suitable for low concentrations of CO<sub>2</sub> (0.04–1.5%)</li> </ul>	<ul style="list-style-type: none"> <li>• Energy-intensive</li> <li>• High capital cost</li> </ul>	<ul style="list-style-type: none"> <li>• Sensitivity to Sulfur compounds and other trace elements</li> <li>• Fouling and low fluxes problems</li> <li>• Excellent low temperature</li> <li>• Excellent H<sub>2</sub> permeability</li> <li>• High resistance to H<sub>2</sub> fluidity</li> <li>• Stable at high temperatures</li> <li>• Resist to impurities</li> </ul>	<ul style="list-style-type: none"> <li>• Less strong permeation ability compared to other metals (V, Nb, and Ta)</li> <li>• High manufacturing cost</li> <li>• Prone to H<sub>2</sub> embrittlement at a low temperature.</li> </ul>
R&D search area	Enhance recovery rate Removal of specific impurity	Enhance purity grade	Mitigate technical challenges	Reduce cost

supports can be monitored with flowmeters which continuously measure hydrogen production before storage [54].

As for hydrogen storage, it is also possible to combine hydrogen trapping by chemical reaction and indirect measurement of the formed compound, such as ammonia (NH<sub>3</sub>, Eq. (1)) [55].



#### « Off-line » analysis

« Off-line » analytical techniques for hydrogen quantification are more frequently used from laboratory to pilot scale, as well as for control or checking measurements in industrial processes. Hydrogen quantification in a gas mixture through GC/MS analysis after gas collection in a cold trap or a bag is the most widespread. This technique will be explained in detail in the Chromatographic techniques section. Hydrogen quantification can also be carried out by pressure measurements, mass flowmeters, or by monitoring the evolved hydrogen into a flow of carrier gas or a vacuum thanks to mass spectrometry (MS) [56].

Thermal Programmed techniques (TPT) allow the dynamic monitoring of a given molecule reacting with a substrate by linearly increasing the reaction temperature and time, which gives information about the chemical functions on the material surface. Thermal Programmed Desorption (TPD), also known as Thermal Desorption Spectrometry (TDS) when MS is used as detector, allows monitoring molecules desorbed from a solid sample with the effect of temperature. It can be applied to determine the hydrogen affinity for the material, by studying its desorption as a function of a thermal ramp [15]. Thermal Conductivity Detection (TCD) is the most usual detection technique coupled to TPD. Recently, Molecular Beam–Thermal Desorption Spectrometry (MB–TDS) was proposed for the in-situ real-time monitoring of hydrogen mass adsorbed in solid storage materials. This system deduces the residual hydrogen background from the total amount of hydrogen detected by the MS, which allows detecting hydrogen traces without a previous calibration, as opposed to conventional TDS. This technique can be applied to accurately determine dehydrating kinetics [57].

« Off-line » hydrogen quantification can also be based on sorption in solid materials, through sorption measurements based on equilibrium isotherms. Thus, hydrogen pressure drop due to sorption, or pressure increase due to desorption, can be monitored with changes in the sample mass (gravimetric methods) or volume (volumetric or manometric methods). As the measurements are related to a given temperature in static conditions, they may present cumulative errors when measuring several isotherms. This is mainly due to the uncertainty in determining pressure and temperature variations, hydrogen compressibility at higher pressures, possible leaks, and volume calibration. Volumetric methods are more usual, as gravimetric ones need buoyancy effect corrections with increasing pressure, which may introduce uncertainty in measurements.

#### « On-line » and « in-line » analysis

In « on-line » measurements, the analyzer is continuously connected to the process through an external line, while « in-line » measurements concern those for which a sensor can be directly placed in a process vessel or flowing gas stream. In « in situ » or « portable » measurements, the analyzer is connected to the process through an external line for one or several discontinuous measurements.

These methods are indicated for process monitoring when a quick answer is expected, as well as when the gas collection is difficult. However, they require robust analytical methods able to provide a quasi-instantaneous response. In counterpart, their precision and reliability can be lower than for off-line methods, especially for low concentrations, so they are not recommended for trace detection [46].

#### Intrusive methods

Intrusive techniques are based on hydrogen quantification by a chemical or photochemical reaction. The main detection and quantification techniques for gas mixtures, valid also for hydrogen, are based on chromatographic, spectrometric, or electrochemical principles.

#### Chromatographic techniques

Chromatographic techniques allow the separation of a complex mixture of liquid or gaseous chemical compounds. The mixed compounds are entrained into the chromatographic column by a mobile phase and separated due to their different affinity with the stationary phase, which is translated in different retention times. The concentration of each compound is proportional to the surface area of the corresponding peak in the resulting chromatogram [15].

Gas chromatography (GC) is an intrusive technique, as the molecule is modified, typically dissociated by ionization. The time required for separation and detection of the mixture compounds implies that GC is considered an « off-line » technique due to the time required for the GC analysis, which may go from several minutes to some hours. Furthermore, if several gas samples need to be analyzed in a continuous process, gas sampling may be necessary. The analysis time can be reduced by the use of hydrogen instead of helium as the carrier gas, which is not compatible with hydrogen analysis [58].

A detection technique needs to be coupled to chromatographic methods to allow compound identification and, if calibration is carried out, quantification [51,59]. The most frequent detection techniques are mass spectrometry (MS), thermal conductivity (TC), and Flame Ionization Detection (FID). However, other techniques such as Thermal ionization detection (TID), helium ionization detection (HID), catalytic combustion detection (CCD), photometric ionization detection (PID), and electron capture detection (ECD) are also used [13].

*Micro-Gas Chromatography (micro-GC).* A special interest was put into the development of portable analytic devices, due to their versatility, robustness, and rapid response for assisting process decisions. Micro Gas Chromatography (micro-GC,

$\mu$ GC) is a miniaturized and portable version of conventional Gas Chromatography (GC). It is considered as « on-line » method as it can provide a quick response, from a few seconds to a few minutes, for a gas mixture containing permanent gases, such as hydrogen.

The main components of a micro-GC are a source of carrier gas, a pre-concentrator-injector, a separation column, a detector, and a pump, controlled by some valves. Software controls data acquisition and analysis [60].

The main advantages of micro-GC are the results accuracy and the fast response (<3 min), which make it suitable for permanent gas monitoring ( $H_2$ , CO,  $CO_2$ , and  $CH_4$ ). However, water vapor and tars typically present in pyrogasification gases need to be removed before micro-GC analysis. Condensable species, including water, can be separated from permanent gases through a cold trap [59,61]. Water can also be removed by a dehumidifier or a drying tube, typically composed of silica gel and  $CaCl_2$  [62].

Nitrogen is used as a standard carrier gas for micro-GC. The measured flow rate can vary from around 40 ml/min [14], or even lower flows in dark fermentation around 10 ml/min [63], to around 600 ml/min in steam gasification [64]. Molecular sieve columns allow the separation of  $N_2$ ,  $CH_4$ ,  $O_2$ ,  $H_2$ ,  $CO_2$ , and other light hydrocarbons. Molecular sieve columns type 5 A or 0.5 nm (MS-5A), by using argon as a carrier gas, are suitable for  $H_2$ ,  $CH_4$ , and CO analysis at 95 °C. Porapak Q (PPQ) or PoraPLOT U columns, using helium as the carrier gas, are suitable for  $CO_2$ ,  $C_2H_4$ , and  $C_2H_6$  analysis at 60 °C [65].

Micro-GC is usually used with Thermal Conductivity Detection (TCD) [13]. TCD is based on the difference in thermal conductivity between the gas to be analyzed and a pure carrier gas, typically helium, contained in two parallel cells. However, helium's close thermal conductivity (0.151 W/(m K)) to that of hydrogen (0.182 W/(m K)) leads to a non-linear conductivity response and signal inversion. A partial replacement of helium by hydrogen (8.5%) as carrier gas leads to hydrogen concentration in the detector above the inversion point, which produces a negative peak for hydrogen that can be easily integrated [66]. The use of argon (0.018 W/(m K)) as a carrier gas is also possible. However, sensitivity with argon will be lower for other permanent gases by a factor of 5–10 [67]. A study about hydrogen detection in exhaust gas from diesel combustion engines showed some uncertainty in hydrogen measurements through TCD. It was shown that TCD was relevantly acceptable for concentrations of about thousands of ppm, but becomes less relevant at lower concentrations [68]. According to manufacturers, micro-GC/TCD detection limit is around 10 ppm and can go down to 0.8 ppm with enhanced configuration and in certain conditions. Miniaturized TCD ( $\mu$ TCD) was developed for portable applications, either separately fabricated from the micro-GC or integrated with a microcolumn. They present a higher sensitivity than conventional TCD, with a detection limit of subparts per million (sub-ppm) [60].

*Gas Chromatography (GC).* Gas Chromatography (GC) is an off-line analytical method for complex mixtures of gases and condensable compounds. It allows analyzing a larger spectrum of chemical compounds than micro-GC, mainly due to its off-line work mode and its larger scale.

GC detection is usually carried out through mass spectrometry (MS) and/or flame ionization detection (FID). While GC-FID quantification is facilitated by the linearity of calibrations, GC-MS is more suitable for the identification of a larger spectrum of chemical compounds, thanks to the MS spectra libraries supplied with GC-MS software. Thus, when coupling GC to MS and FID, MS is typically used for identification and FID for quantification [69]. The off-line use of GC-FID or GC-MS is combined with a gas capture system, which may be a cold trap for condensable species or a collector bag for gaseous samples. However, when coupling GC and MS, hydrogen analysis is not possible as there is any carrier gas lighter than it. The particularity of hydrogen analysis by GC-MS is based on the generation and detection of  $H_2$  isotopes by low-pressure chemical ionization MS with Electron Ionization (EI) ion source and the monitoring of the protonated carrier gas [70]. In general, hydrogen analysis through GC and possibly with a Helium Ionization Detector (HID), an Atomic Emission Detector (AED), and a TCD, which is the most frequently used configuration.

Flame Ionization Detectors (FID) present high sensitivity based on the molecule's ability to be ionized thanks to a hydrogen-air flame. FID is insensitive to most GC carrier gases, as well as air, water, ammonia, carbon dioxide, hydrogen sulfide, sulfur dioxide, and hydrogen. However, FID is sensitive to compounds containing hydrogen and carbon. The electrical conductivity of the flame is in particular sensitive to organic vapors, with a detection limit of around 20 pg per component [71]. FID sensitivity depends on combustion and carrier gas flow rates, flame jet exit diameter, relative positions of jet and collector, and, to a minor extent, detector temperature. Typically, the  $H_2$ :air flowrate ratio for FID combustion is 1:10 (around 30–45 ml/min of  $H_2$  and 300–450 ml/min of air). Hydrogen quality for FID should be of 99.995% purity, or 99.999% when it is used as a carrier gas; in both cases, hydrocarbon impurities must be below 100 ppb. Temperature detector recommendations are between 20 and 50 °C higher than the maximum operating temperature of the column but lower than 150 °C. This may avoid noise generation and condensation of steam produced while ensuring stable detector operation [72]. As FID requires an external source of hydrogen for the flame, its use in portable devices is still limited [60]. Some signs of progress were made in miniaturizing FID devices ( $\mu$ FID, miniaturized FID) by reducing the required hydrogen flow thanks to the use of a capillary GC column as the flame cell [73].

Hydrogen gaseous pollutants can be analyzed using GC techniques. GC/FID with helium as a carrier gas and a Porous Layer Open Tubular (PLOT) column is suitable for light hydrocarbons (up to 2 carbon atoms), including methane, with a detection limit of 1 ppmv for methane, 1.6 for ethane, 2.9 for propane, 4 for butane and 5 for pentane. GC-MS/FID coupled to a TD (thermal desorption) is suitable for hydrocarbons heavier than propane, with a detection limit of 0.05 ppm per hydrocarbon when sampling 100 ml hydrogen on sorbent tubes packed with a strong molecular sieve [69,74].

When analyzing trace impurities in high-purity hydrogen gas, Pulsed Discharge Detector (PDD), also named Pulsed Discharge Helium Ionization Detector (PDHID), avoids overlapping between the hydrogen GC peak and peaks from trace

compounds. The discharge gas in the PDD, typically helium, is separated from the carrier stream, so the bulk of the matrix peak never enters the discharge region and trace compounds can be better distinguished. The detection limit of PDD was revealed to be an order of magnitude lower than that of conventional FID and TCD (0.3 ppmv). In general, PDD is 500 times more sensitive than TCD and 50 times more sensitive than FID. When dealing with High-Speed Gas Chromatography (HSGC), PDD showed a sensitivity equivalent to that of FID, but a higher sensitivity than that of TCD [75]. A miniaturized version of PDD was proposed (Valco), especially suitable for portable applications due to its reduced size and helium consumption, for an equivalent sensitivity to that of standard PDD (about 100 ppb for permanent gases) [76].

A specific device was proposed for fast and accurate measurement of hydrogen purity through the determination of the main pollutants for fuel cells, according to ISO14687. This includes O<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, Ar, CH<sub>4</sub>, and other hydrocarbons such as ethane, propane, butane, isobutane, methanol, ethanol, and acetone. It combines three GC columns, including two packed columns, a PLOT column, and two detectors (FID and TCD) coupled in parallel to two OFCEAS (Optical Feedback Cavity Enhanced Absorption Spectroscopy) instruments using reference gas mixtures. Analysis time is estimated to be 1 h and the method accuracy agrees with standard thresholds [77].

#### *Spectrometric techniques*

Spectroscopic techniques are based on the interaction of matter and radiated energy. Spectrometric techniques refer to the measurement of these interactions, through radiation intensity and wavelength.

The most common spectrometric technique for permanent gas detection is Mass Spectrometry (MS), suitable for hydrogen detection. Fourier Transform InfraRed Spectroscopy (FTIR), typically used in permanent gas detection in combustion [15], cannot detect noble or diatomic gases, such as hydrogen, as they do not have absorbance bands in the infrared region of the spectrum.

*Mass spectrometry (MS).* Mass spectrometry (MS) is a suitable technique for the « in-line » identification and quantification of hydrogen. It consists of the evaporation, ionization, and fragmentation of the sample to obtain ion fragments that are classified as a function of their mass-to-charge ratio ( $m/z$ ). In the spectrum, the signal at the highest  $m/z$  corresponds to the molecular ion. The ionization process is known to be depth for most permanent gases (hydrocarbons, CO<sub>2</sub>, CO, H<sub>2</sub>) and volatile species. This allows their identification by comparison of the fragments to those from the database. Electron Ionization (EI) is frequently used for permanent gas analysis, while new techniques such as Electrospray Ionization (ESI) and Matrix-Assisted Laser Desorption/Ionization (MALDI) allow the analysis of biological complex systems [78]. The high sensitivity of MS is translated in a very low mass of sample required, less than 1 µg, and even lower in trace analysis (about 1 pg). That is the reason why MS is not completely considered a destructive technique.

The  $m/z$  overlapping of the gas releases in the MS spectrum is frequent in the analysis of permanent gases released from

biomass conversion. This implies that each  $m/z$  corresponds to several gas species, which makes difficult their identification. To overcome this limit, curves of relative intensities are analyzed which allow distinguishing  $m/z$  from different gases whose concentration is at a different order of magnitudes [79].

It was shown that the ion current (absolute intensity) is proportional to gas concentration, which allows quantifying single and well-known compounds in concentrations below 0.2 to 0.5 wt% thanks to calibration [80]. However, this method is not easily applicable to complex mixtures of permanent gases as it requires the determination of a specific calibration factor for each compound in the selected carrier gas related to a well-known compound, such as calcium oxalate, in the given gas mixture [81]. Even if some semi-quantitative methods were proposed [79], MS analysis remains mainly qualitative unless calibration is made with a given gas at well-defined conditions [82].

Ensuring a linear response of the MS instrument is challenging when heavy and/or noble gases are mixed with light gases such as hydrogen at different concentration levels. Moreover, MS carrier gas needs to be carefully chosen, as it may be decomposed in fragments coincident with those of the gases to be analyzed. When syngas is analyzed, argon may be preferred to N<sub>2</sub>, to avoid  $m/z$  fragment 28 which also corresponds to CO [79]. Furthermore, several ionization energies may be used to distinguish the signature of some fragments that present a close behavior, such as water and ammonia [83].

Quadrupole Mass Spectrometry (QMS) was pointed out as the most sensitive technique for gas composition analysis. However, the sensitivity of the instrument for a given chemical compound, usually tested in a large range of pressures with noble gases, is dependent on the concentration of other species in the gas mixture. Recent studies pointed to quantification inaccuracy, especially when dealing with low concentrations and/or mixtures of heavy and light gases [84]. In this case, Leckey and Boeckmann proposed a complex method based on the implementation of a control valve to maintain constant low pressure in the QMS analytical chamber. However, QMS response time needs to be integrated to calculate sample composition [85]. To simplify gas composition determination, Zajec et al. proposed the quantification of partial flow rates into the analytical chamber of the QMS, to determine the gas composition in the batch inlet [86]. Nevertheless, QMS drawbacks remain slow response, non-linearity, and interference even at low ion current readings.

Ion trap mass spectrometer (ITMS) covers the same area of selective gas detection as the QMS with a faster response [87]. The limitations on its ability to determine small gas concentrations were shown for a mixture of hydrogen and noble gases. In this case, hydrogen was highly underestimated [88]. This study suggested that a combination of QMS and ITMS methods would simplify and improve the quantification of small amounts of gas [88].

In biomass conversion processes at the lab scale, MS can be coupled with thermogravimetric analysis (TGA) for the online study of permanent gases, including hydrogen. The advantages of this MS technique for gas analysis are the real-time response and the sensitive detection of the most important permanent gases [82]. Coupling MS profile and TGA curves allow linking dehydrogenation reactions with biomass macromolecular

components decomposition [79]. TGA-MS was also used for the study of hydrogen storage in solid materials, such as magnesium alanate [89] and hydrogenated graphene [83].

GC-MS can reach the detection limit for permanent gases such as CH<sub>4</sub>, O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub> as specified in ISO14687-2 for hydrogen fuel for PEMFC use in vehicles. Detection limits are defined for CH<sub>4</sub> (2 ppmv), CO<sub>2</sub> (2 ppmv), Ar (100 ppmv), O<sub>2</sub> (5 ppmv), N<sub>2</sub> (100 ppmv), and CO (0.2 ppmv). The low detection limit for H<sub>2</sub>S (1 ppb-vol) leads to the use of specific detection techniques, such as sulfur chemiluminescence detection (GC-SCD). Standard techniques, such as TD-GC/MS, would not easily allow reaching this limit [69,74].

#### *Electrochemical techniques*

Electrochemical analytical techniques are based on chemical reactions involving electrical charges and are carried out in an electrochemical cell. This device is composed of two electrodes, among which a current is applied, separated by a non-conductive membrane. The measurement principle is amperometry, which is related to the current generated by reduction-oxidation (redox) reactions.

Electrochemical techniques for hydrogen analytics are related to electrochemical-based sensors. These sensors are a proven technology of affordable cost. They are gas-specific in a ppm range, present a linear output, low power requirements, good resolution, excellent repeatability, and accuracy once calibrated. However, electrochemical sensors are sensitive to temperature. They have a limited life (6–12 months), which can be shortened by the presence of moisture and/or other gases.

Grimmer et al. proposed an electrochemical method for hydrogen real-time quantification based on the electrochemical oxidation of hydrogen in a mixture of dry or humid gases produced in dynamic conditions. His electrochemical cell was composed of a test electrode, to which the gaseous mixture containing hydrogen was supplied, and a counter electrode, fed with a known flow of hydrogen and acting as the reference. This method was successfully tested in the steam iron process, as well as in the catalytic hydrolysis of borohydride for hydrogen storage. The limit of quantification in the test cell was 0.30 ml (H<sub>2</sub>).min<sup>-1</sup> for maximal hydrogen flow investigated of 100 ml (H<sub>2</sub>).min<sup>-1</sup> [90].

Electrochemical, spectrometric techniques, such as Rutherford backscattering spectrometry [91], and potential distribution techniques are more frequently used for hydrogen detection and quantification on the surface of solid materials [92].

#### **Non-intrusive methods**

Most of the non-intrusive techniques are deployed by the mean of sensors based on different physicochemical measurements where the hydrogen molecule is not destroyed. They are directly placed in the gas lines in the process and need to respond rapidly, be accurate, sensitive to hydrogen and insensitive to other gaseous species, and resistant to long-term drift and environmental conditions. With a Lower Flammability Limit (LFL) of just 4.0 vol% in air, detection of

hydrogen is required at low concentrations usually specified at either 10% LFL (0.4 vol%) or 25% LFL (1.0 vol%) [46].

#### *Mass flowmeters and controllers*

Flow controllers and flowmeters allow continuous data acquisition for a given gaseous specie. Mass flow controllers also allow the modification of mass flow thanks to an integrated valve. In both cases, the presence of moisture limits their reliability, and the quantification is difficult for gas mixtures. The explosive nature of hydrogen implies that explosion-proof flowmeters need to be selected and oxygen cannot be measured through the same device to avoid combustion [90].

In general, several types of flowmeters are proposed in the market for hydrogen measurements, including thermal mass flowmeters, (precision) vortex flowmeters, and ultrasonic gas flowmeters. Thermal and Coriolis mass flowmeters are especially suitable for trade settlement and measurement due to their excellent detection technology, leading to high accuracy, dependent on the flow rate measurement range. Thermal mass flowmeters directly measure mass flow based on the thermal diffusion of gases. Coriolis mass flowmeters are based on the Coriolis principle, according to which the mass flow momentum of a fluid (gas or liquid) changes the vibration of a fixed tube when passing through it, which is translated in a measurable phase shift and a linear output derived proportional to flow.

Ultrasonic gas flowmeters are based on the determination of the velocity of a liquid or a gas through a pipe by the measurement of ultrasonic sound waves (Doppler effect). They fit for applications where chemical compatibility, low maintenance, and low-pressure drop are required. Ultrasonic mass flowmeters developed for biogas can determine the methane content with high accuracy (1% error of measured flow value and 2% of methane content), regardless of the moisture content and the impurities in biogas, such as H<sub>2</sub>S (Optisonic, Krohne).

Magnetic flowmeters measure the volumetric flow through the speed of a fluid passing through a pipe. They are based on the principle according to a liquid is a source of voltage when flowing through a magnetic field (Faraday's Law of Electromagnetic Induction). However, a temperature and pressure sensor is required to correct the volumetric flow regarding the standard state. The wide range of temperatures and pressures for hydrogen implies a high variability in the corrected volume and thus considerable uncertainty, which measurement is not especially recommended for hydrogen.

Lab-made hydrogen flowmeter was proposed by Lacomte et al. based on the correlation between mass flow rate and upstream gas pressure, for a gas flow that is released through a calibrated orifice (shocking flow principle). A variation in the orifice size (5–20 mm) allowed setting mass flow between 5 mg/s and 10 g/s in an experiment predicting hydrogen dispersion in confined spaces [93].

Commercial hydrogen mass flowmeters and controllers are available in low (up to 10 l/min), medium (100 l/min), and high (1000 l/min) flow range relative to nitrogen (Dakota,

Bronkhorst, 3 M). They may work at a maximum gas pressure of 35–70 bar, leading to accuracy between 1% and 3% at full scale, with a maximum pressure drop of up to 1 bar for flowmeters of flow rate range up to 1000 l/min [94]. Some recent mass flowmeters can operate up to 1400 bar, in a large range of temperatures (from about  $-253\text{ }^{\circ}\text{C}$  to  $350\text{ }^{\circ}\text{C}$ ). Coriolis mass flowmeters are proposed for a large range of mass flow, from around 1 g/min (micro-flow) to 30 tons/min. Thus, they are especially appropriate for the high flow rate range, due to their high precision ( $<0.15\%$ ; RHEONIK, METRA). These flowmeters are insensitive to impurities and moisture, due to their monobloc-stainless-steel structure without moving parts, seals, or welding areas. However, their main drawbacks are their high cost and insensitiveness to changes in viscosity, temperature, and pressure. Thermal mass flowmeters prices are much more affordable. They are typically preferred for measuring smaller flow rates at low pressure. However, as they are affected by variations in density, temperature, and pressure, they require a real flow for calibration, to reach high accuracy ( $<1\%$  for  $100\% \text{H}_2$ ).

The supply of high-pressure hydrogen is currently an important point in the implementation of hydrogen in the transportation sector. Gravimetric and volumetric techniques, together with mass flowmeters, were proposed to periodically check hydrogen dispensers at hydrogen fueling stations. The gravimetric technique is based on weighing a pressure vessel before and after filling. The volumetric technique follows the same methodology, but it is based on a difference in volume. In this case, the heat of compression makes it difficult to obtain an average gas temperature with acceptable uncertainty [95]. It was shown that the accuracy of Coriolis mass flowmeters in the dynamic filling process at different pressures and short refueling times was insufficient according to legal requirements. To overcome this limit, manufacturers implemented pressure and temperature corrections on their devices, which were tested in a wide range of pressures (10 MPa–85 MPa) and flow rates ( $0.1\text{ kg min}^{-1}$  to  $3.6\text{ kg min}^{-1}$ ) [96]. Furthermore, a specific calibration facility was proposed for a Coriolis flowmeter in the pressure range of 15–35 MPa, with a relative standard uncertainty of the mass flow rates of 0.09% when the flow rate is between 150 g/min and 550 g/min [97]. Nowadays, there are few analytic devices specifically designed to accurately measure high-pressure hydrogen gas flow rate during supplying, such as Critical Flow Venturi (CFV, uncertainty  $<0.13\%$ ) [95].

### Sensors

Hydrogen sensors are transducer devices used in monitoring and leak detection. They transform a change detected by the sensing element (temperature, refractive index, electrical properties, mass, and mechanical changes) into an electrical signal whose magnitude is proportional to the hydrogen gas concentration detected. Hydrogen sensors are adapted for stationary applications, portable and in situ detection, due to their smaller size, lower cost, and faster response compared to other in-line methods. They require periodic calibration to ensure the sensor's performance stability with time.

Hydrogen sensors were developed about a century due to their crucial role in diverse processes such as coal,

petrochemistry, ammonia and methanol synthesis, as well as nuclear energy [98]. The principles on which are based sensors for combustible and explosive gases are valid also for hydrogen sensors. The detection and quantification of hydrogen concentration can be related to the reaction itself (reaction heat) or changes in the properties of the sensing material (resistance, volume expansion, etc.).

Hydrogen sensors can be based on physical changes induced in a noble metal, such as Pt, due to its ability to adsorb hydrogen. Thus, work-function, resistive, and capacitive hydrogen sensors are based on variations on the work-function, electrical resistance, and stress of the noble metal due to hydrogen adsorption, respectively. Even if capacitive hydrogen sensors present a lower power consumption, the main drawbacks of these sensors are their long response time, mainly due to the difficulties to release the adsorbed hydrogen, and hysteresis problems. A limit of these materials is their ability to adsorb hydrogen, which may lead to mechanical damage to the sensor [99].

Specific interactions of hydrogen with noble metals (platinum, palladium) related to catalytic reactivity and solubility allowed to development of selective hydrogen sensors. They are typically composed of semiconductors, such as  $\text{SnO}_2$ ,  $\text{WO}_3$ ,  $\text{TiO}_2$  and  $\text{ZnO}$ , generally doped with noble metals (Pt, Pd). New conductimetric gas sensors based on pure zirconium oxide ( $\text{ZrO}_2$ ) or doped with yttrium oxide ( $\text{Y}_2\text{O}_3$ ) were recently proposed for the detection of low  $\text{H}_2$  concentrations ( $<100\text{ ppm}$ ) [100].

Sensors' response time is typically given as T50 and T90, which corresponds to the time consumed when the gas detector changes from reading 0–50% or 90% of the measured gas concentration, respectively. This response time depends on the specificity of the hydrogen sensor, or its generic use for diverse explosive gases. It can go from a few seconds to a minute for T90, and it is generally below 30s for T50. It was shown that the fastest response times were obtained with electronically switched solenoid valves or a pneumatic switched test chamber [101].

Sensors for detecting hydrogen leaks typically work at atmospheric pressure, from 0 to 2000 ppm (Honeywell, 3 M) and from around  $-20$  to  $50\text{ }^{\circ}\text{C}$ . They admit 15 to 90 wt% relative moisture, without condensation, and their accuracy is around 5 wt%. Sensors for hydrogen monitoring exist for a wide range of concentrations (from 0.1 to 100 vol%), with an accuracy of 0.1–10 vol% of the indicated value (up to 30 vol% in some cases) and a response time (T90) between 2 and 90 s [98].

Hydrogen concentration and application determine the most suitable sensor technology. Electrochemical and semi-conducting metal–oxide sensors fit for low hydrogen concentration measurements, due to their acceptable selectivity, while robust catalytic and low selectivity thermal conductivity sensors are preferred at higher hydrogen concentrations [98]. When monitoring hydrogen in a gaseous matrix, the presence of the other gases may impact the measurement. Recently, a platinum-based hydrogen sensor was proposed for hydrogen monitoring during its injection in the current natural gas network. The sensor, which presents a high accuracy (0.1 vol %) and reversibility, can be integrated in natural gas and

**Table 2 – Advantages and disadvantages of the main analytical methods for hydrogen detection, quantification, and monitoring [69,103].**

Technology	Detection system/device type	Advantages	Disadvantages
Intrusive methods Micro-gas chromatography ( $\mu$ GC)	Thermal conductivity detector (TCD)	<ul style="list-style-type: none"> <li>• robust and mature technology</li> <li>• low power consumption</li> <li>• fast-answer (&lt;3 min)</li> <li>• accurate results</li> <li>• suitable for permanent gases monitoring</li> <li>• suitable for quantification (linear response)</li> </ul>	<ul style="list-style-type: none"> <li>• sensitive to water and tars (need to be prior removed)</li> <li>• calibration required</li> </ul>
	Flame Ionization detector (FID)	<ul style="list-style-type: none"> <li>• very sensitive for most organic compounds (ppb)</li> </ul>	<ul style="list-style-type: none"> <li>• FID only responds to C–H bonds (not suitable for H<sub>2</sub>)</li> <li>• low sensitivity for small molecules (N<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>S)</li> <li>• calibration required</li> </ul>
	Pulsed Discharge Detector (PDD) or Pulsed Discharge Helium Ionization Detector (PDHID)	<ul style="list-style-type: none"> <li>• lower detection limit than TCD, FID</li> <li>• higher sensitivity than TCD, FID</li> <li>• higher sensitivity in high-speed GC</li> <li>• reduced size and He consumption in miniaturized versions</li> </ul>	<ul style="list-style-type: none"> <li>• complex and expensive technologies</li> </ul>
Mass spectrometry (MS)	Quadrupole Mass spectrometer (QMS)	<ul style="list-style-type: none"> <li>• high sensitivity for a single compound</li> <li>• very low mass of sample required (non-destructive)</li> </ul>	<ul style="list-style-type: none"> <li>• inaccuracy in low concentrations and/or mixtures of heavy and light gases</li> <li>• calibration required</li> <li>• mainly qualitative</li> <li>• slow response</li> <li>• non-linearity</li> <li>• interference even at low ion current readings</li> </ul>
	Ion trap mass spectrometer (ITMS)	<ul style="list-style-type: none"> <li>• high sensitivity for a single compound</li> <li>• very low mass of sample required (non-destructive)</li> <li>• faster response than QMS</li> </ul>	<ul style="list-style-type: none"> <li>• limitations when determining small gas concentrations for a mixture of H<sub>2</sub> and noble gases</li> <li>• calibration required</li> <li>• mainly qualitative</li> <li>• non-linearity</li> </ul>
Electrochemical techniques (sensors)		<ul style="list-style-type: none"> <li>• gas-specific in a ppm range</li> <li>• linear output</li> <li>• low power requirements</li> <li>• good resolution</li> <li>• excellent repeatability and accuracy</li> </ul>	<ul style="list-style-type: none"> <li>• require calibration</li> <li>• sensitive to temperature</li> <li>• narrow or limited temperature range</li> <li>• limited life (6–12 months)</li> <li>• sensitive to the presence of moisture/other gases</li> </ul>

Non-intrusive methods			
Mass flowmeters and controllers	Thermal mass flowmeter	<ul style="list-style-type: none"> <li>• mature technology</li> <li>• linear output proportional to flow</li> <li>• suitable for trade settlement and measurement</li> <li>• high accuracy</li> <li>• lower price than Coriolis mass flowmeters</li> <li>• preferred for smaller flow rate measurements and low gas pressure</li> </ul>	<ul style="list-style-type: none"> <li>• real flow required for calibration to accurately measure the H<sub>2</sub> flow rate</li> </ul>
	Coriolis mass flowmeter	<ul style="list-style-type: none"> <li>• linear output derived proportional to flow</li> <li>• especially suitable for trade settlement and measurement due to its high accuracy</li> <li>• excellent performances for high flow rate range</li> <li>• insensitive to moisture and impurities (monobloc-stainless-steel structure)</li> </ul>	<ul style="list-style-type: none"> <li>• large pipe diameters required</li> <li>• high prize</li> <li>• insensitiveness to changes in viscosity, temperature, and pressure</li> </ul>
	Ultrasonic mass flowmeter	<ul style="list-style-type: none"> <li>• suitable for applications requiring chemical compatibility, low maintenance, and low-pressure drop</li> <li>• simultaneous determination of H<sub>2</sub> flow and purity</li> </ul>	<ul style="list-style-type: none"> <li>• high prize</li> <li>• specific maintenance</li> <li>• H<sub>2</sub> flow and purity simultaneous measurement under development</li> </ul>
	Magnetic mass flowmeter	<ul style="list-style-type: none"> <li>• mature technology for permanent gases</li> </ul>	<ul style="list-style-type: none"> <li>• insufficient accuracy for H<sub>2</sub> quantification with pressure/temperature</li> </ul>
Sensors	Direct sensors	<ul style="list-style-type: none"> <li>• large range of concentrations</li> <li>• small size</li> <li>• mature technology</li> <li>• low cost</li> <li>• portable, in situ, and stationary applications</li> </ul>	<ul style="list-style-type: none"> <li>• variable response time and accuracy</li> <li>• moisture limits reliability</li> <li>• quantification difficult for gas mixtures</li> <li>• periodical calibration required</li> </ul>
	Indirect sensors (O <sub>2</sub> )	<ul style="list-style-type: none"> <li>• mature</li> <li>• commercially available technology</li> <li>• easy to calibrate with ambient air or inert gas</li> <li>• simple to use</li> <li>• broad linear detectionrange</li> <li>• quick response (&lt;1 s for some models in certain conditions)</li> </ul>	<ul style="list-style-type: none"> <li>• low accuracy in detecting low H<sub>2</sub> concentrations</li> </ul>

**Table 3 – Performances of the main analytical methods for hydrogen detection, quantification, and monitoring.**

	Technology	Detection/ device type	Concentration range (H <sub>2</sub> )	Accuracy for H <sub>2</sub>	Temperature range	Pressure range	Response time	Moisture admitted
Intrusive methods	μGC	TCD	>0.3 ppmv	0.8–10 ppm (< ppm μTCD)	Ambient T	<2 bar	<3 min	no
	GC	FID	>0.3 ppmv	low ppb to high ppt				yes
		PDD/PDHID			100 ppb			yes
Non-intrusive methods	MS	FID, MS	50 %vol	low ppb to high ppt			1–10 min	yes
		QMS	100 ppm-100 vol%	low ppb			10 ms	yes
	Electrochemical techniques	ITMS	>0.1 wt% >0.3 ml					yes
				(H <sub>2</sub> /min in 100 ml (H <sub>2</sub> flow)/min [90])				
Non-intrusive methods	Mass flowmeters/ flowcontrollers	Thermal	0–1000 l/min	1–3%	–253 °C–350 °C	<35/70 bar	2 s	yes
		Coriolis	1 g/min to 30 tons/min	0.1–0.15% of Qmax or Qmin		<1400 bar	10 ms	
	Sensors	Direct sensors	0.1 to 100 %vol	0.1–10% vol	–20 to 50 °C	Atm P	<30s (T50) 2–90 s (T90)	Limited (15–90% relative moisture)
		Indirect sensors (O <sub>2</sub> )					<1 s	

biogas sensors, being able to assess the full gas composition [102].

Semi-conductor sensors, based on redox or adsorption reactions, are frequently used in research applications. MEMS (Micro-Electro-Mechanic System) combines calculators and minuscule devices such as sensors, valves, mirrors, and actuators, loaded on a semi-conductor chip. They are used in aeronautic and spatial industries [103]. Recent developments in hydrogen sensors include metal–oxide nanostructures, carbon nanotubes, and palladium nanoparticles, as well as fiber optics and more performant semi-conductors (based on GaAs, GaN, InN, or SiC, but also doped Si nanowires) and Schottky diodes [98,103]. The development of resistive nanostructured hydrogen sensors based on metal oxides, transition metal dichalcogenides and graphene is crucial for proposing sensors able to operate at low temperatures (<200 °C) [104].

Some studies proposed the adaptation or the development of specific analytical solutions for hydrogen leak detection and monitoring. In this sense, a portable hydrogen gas leak de-tector based on Coherent Anti-Stokes Raman Spectroscopy (CARS) was proposed. Its response time is 1s and the detection range is from 200 ppm to 100%vol, at temperatures between 0 and 30 °C. This method, based on the strong Raman effect showed by hydrogen, intends to cope with the need for a fast response, which may be challenging for the gas suction type sensors [105]. Other selective hydrogen leak conductometric sensors based on doped transition metal ions (Mn, Co) were proposed for automotive applications [106]. Finally, the determination of liquid hydrogen leaks (cold hydrogen plumes) appears to be crucial for the growth of the use of hydrogen in transportation sectors, such as aeronautics. In this sense, the National Renewable Energy Laboratory (NREL) Sensor Laboratory at the United States developed the Hydrogen Wide Area Monitoring (HyWAM). This system is based on a distributed array of point sensors and is able to identify planned or unintentional liquid hydrogen releases. HyWAM uses hydrogen TC sensors with a broad, nearly linear measurement range (from 0 to 100 vol% H<sub>2</sub>), low detection limits (ca. 0.1 vol% H<sub>2</sub>) and fast response time (T90 < 250 ms) [107].

The use of indirect sensors for hydrogen measurements related to other gases such as oxygen was also proposed. For instance, a decrease in oxygen level could be measured by the oxygen sensor when air is displaced by a diluent gas, such as hydrogen. Oxygen sensors are mature and commercially available, easy to calibrate with ambient air or inert gas, simple to use, and present a broadlinear detection range and a quick response (<1 s for some models in certain conditions). However, the accuracy of these sensors in detecting low hydrogen concentrations may be insufficient [108]. The United Nations, through the Global Technical Regulation (GTR) on hydrogen and fuel cell vehicles, supported this method to verify the integrity of hydrogen vehicles' fuel cell systems [109].

## Conclusions

The deployment of hydrogen production from biomass and biowaste at a larger scale (TRL >7), as well as the integration of

hydrogen production in a biorefinery approach, will contribute to lower hydrogen price. This should enable and accelerate the replacement of grey hydrogen by bio-hydrogen in industrial, energy and transport sectors. However, hydrogen monitoring and quantification are crucial to optimize the effectiveness and ensure the reliability of the hydrogen value chain, especially when handling complex gas mixtures containing hydrogen, which is the case of hydrogen production from biomass and biowaste.

This review proposes a synthesis and critical analysis of the existing analytical techniques and the associated tools available in the market for hydrogen detection, quantification, and monitoring, as summarized in Table 2. Their application domain is directly related to their precision, response time, and technical limitations that impact their cost, as provided in Table 3. Selecting the most suitable technique is directly related to hydrogen composition and application. This selection may be mainly dependent on the analysis mode (on-line, in-line, or off-line), the impact on the hydrogen flow (intrusive or not), the presence of other gases, the concentration of hydrogen, the required response time, the acceptable uncertainty, the operating conditions (temperature, pressure, moist environment) and the cost.

The production of hydrogen from renewable resources concerns not only electrolysis, which directly produces high-grade hydrogen, but also bioresources transformation, whose the potential at the local scale, where electrolysis may be challenging to handle, may play a significant role in the widespread use of hydrogen technologies and thus the reduction of its cost. Analytical techniques need to be able to provide a precise, fast and reliable quantification of hydrogen in a complex matrix of diverse pollutants, and this is throughout the whole process of hydrogen production, separation, purification, and end-point application. As a result, robust monitoring of hydrogen purity may allow optimizing the cost of its production and purification according to the targeted purity of the end-point application, and thus will contribute to gaining security on its final use.

## Future research directions

Among the main challenges in hydrogen analytics, the determination of the detection limit and the sensitivity of the instrument or detection technique are crucial. They are dependent on the gaseous mixture analyzed and on operating conditions. Most of the fabricant data sheets for instruments do not indicate the specific detection limit for each gaseous specie, but a general value, as for micro-GC/TCD. The use of reliable standards for calibration, representative of the matrix effects in gaseous mixtures, would be crucial to provide an accurate measurement. However, the availability of these standards in the market is still scarce and their price is onerous. The complex thermodynamic behavior of hydrogen may represent a challenge for sensors and flowmeters based on volumetric measurements.

The selection of an analytical technique should be made according to the gas concentration to be determined, the gas purity to be achieved, the impurity threshold, and the nature of the given hydrogen applications. This is especially relevant when quantifying pollutants on a hydrogen flow for applications requiring a high degree of purity. For example, the detection limit for CO<sub>2</sub> can go from 2 to 5 μmol/mol for GC-TCD to 0.015 for GC-PDHID or mechanized GC-FID, while the threshold in ISO 14687 is 2 μmol/mol for PEMFC in road vehicle applications [74]. Recent developments based on ultrasonic gas flowmeters for biogas were adapted to the simultaneous quantification of hydrogen flow and main impurities (KROHNE). Furthermore, a device under development combines an ultrasonic gas flowmeter and a concentration sensor for the simultaneous measurement of hydrogen flow rate and concentration in a humid environment (Panasonic, 0 to 700 NL/min and 2% accuracy for 100% H<sub>2</sub>, with N<sub>2</sub> and O<sub>2</sub> as impurities, 0–70 °C, up to 5 bar). In a couple of years, such an application will represent a step beyond the state-of-the-art as moisture content has always been among the key issues in gas and particularly hydrogen analysis.

In the transportation sector, for instance, hydrogen sensors need to be able to alert from unintended hydrogen releases before reaching explosive conditions. In this case, low hydrogen concentration was stated as 10% of the LFL (0.4 vol %) for devices ensuring public safety [46]. The main challenges identified in the introduction of hydrogen in vehicles are directly related to analytical measurements, namely flow meter types of equipment, quality assurance, quality control, sampling and accurately measuring flow rate when supplying high-pressure hydrogen gas in refueling stations [110].

The reactivity and the high adsorption of hydrogen with other gases with strong chemical bonds of solid materials could be an issue in the detection limit, response time, and accuracy of the measurements. The development of materials with an easy adsorption-desorption cycle of hydrogen under measurement conditions could improve and widen the range of hydrogen detection and measurement techniques. This is related to the development of solid materials with higher volumetric and gravimetric hydrogen density, which is attracting important attention from the research community, industry, and regulatory bodies.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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