Analysis of Bio-H$_2$ Production Routes from Biomass Gasification

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The use of hydrogen (H$_2$) as an energy carrier may have an important role in the near future. Nowadays, H$_2$ is mostly produced from fossil fuels, thus, it is urgent to prove the viability of alternative and sustainable processes to obtain H$_2$. Gasification of renewable sources like biomass that are widely available, inexpensive and carbon-neutral is considered a viable technical, economic and environmental alternative for H$_2$ production. The first step of biohydrogen (bio-H$_2$) production through biomass gasification is the production of syngas (gasification gas). Syngas cleaning and upgrading procedures are essential to remove undesirable compounds and to increase bio-H$_2$ content. Steam reforming and water gas shift reactions are also crucial to increase bio-H$_2$ content in syngas. Next, bio-H$_2$ separation from other gaseous compounds is needed to finally obtain bio-H$_2$ at the required purification level. Although some of the mentioned technologies are proven and available on the market for similar applications, some drawbacks and technological challenges for the overall process need to be overcome to improve the overall techno-economic feasibility. This paper aims to analyse and discuss different bio-H$_2$ production routes from biomass gasification to c the most promising ones.

1. Introduction

Gasification is a thermochemical conversion process that is suitable to convert a wide range of feedstocks (sewage sludge, forestry biomass, agro-industrial wastes, energy crops, plastics mixtures, used tyres, RDF (refuse derived fuel), MSW (municipal solid waste), etc.) into syngas. This gas contains H$_2$, carbon monoxide (CO), carbon dioxide (CO$_2$), gaseous hydrocarbons, mainly methane (CH$_4$), tar and other minor components, like NH$_3$, H$_2$S, etc. Gasification main advantages are high fuel conversion and flexibility, as mixtures of different feedstocks may be gasified. However, as there is a rising interest in gasifying poor quality materials and some may contain high amounts of undesirable elements that may form pollutant precursors, some of the most interesting syngas utilizations are limited or difficult, unless suitable syngas cleaning and upgrading procedures are used. There are several biomass gasification technologies with the possibility of gasification integration with other technologies.

Gasification gas may be used in different sectors like heat and power generation, transport fuel and chemicals production, and bio-H$_2$ production. Thus, nowadays gasification main research areas besides bio-H$_2$ production (see, for instance, Cao et al., 2020) are the production of SNG (synthetic natural gas) to substitute fossil natural gas, as well as the capture, storage and utilization of CO$_2$ from gasification process - Bio-Energy Carbon Capture Utilization and Storage (BECCUS). Another important subject is syngas utilization to produce biofuels and biochemicals, instead of only CHP (combined heat and power) applications. Syngas is used in chemical synthesis like FT (Fischer–Tropsch) to obtain liquids (kerosene, diesel, gasoline) or to produce bio-DME (dimethyl ether) to be used in long-distance transportations (Sapariya et al., 2021).

This paper revises and analyses the main technological processes to convert syngas into bio-H$_2$, by different production routes with the aim of pointing to the most promising ones.

2. Technology assessment

Biomass gasification has been widely studied and there are different technologies available. In autothermal gasification, oxygen or air is used for heat production by partial oxidation, while in allothermal gasification, the heat needed for gasification reactions is supplied by an external source. In Table 1 are summarised the main conventional biomass gasification technologies, considering gasifier type and typical operating conditions.

Table 1: Biomass gasification technologies (Costa et al., 2021).

Gasification Technology	Main Operating Conditions
Fixed Bed Gasifier	
Downdraft	Outlet Gas Temperature: ~ 500ºC
Updraft	Reaction time: ~ minutes
Crossdraft	Particle size: 5 – 50 mm
Fluidized Bed Gasifier	
Bubbling Bed	Outlet Gas Temperature: 700 – 900ºC
Circulating Bed	Reaction time: 5 – 50 s
	Particle size: 0.5 – 5 mm
Entrained Flow Gasifier	
	Temperature: 900 – 1400ºC
	Reaction time: 5 – 50 s
	Particle size: < 500 µm

For some end-uses, like bio-H_2 production, syngas has to be free of nitrogen, so oxygen has to be used instead of air in the partial oxidation, or allothermal gasification technologies should be selected, as those presented in Table 2. These gasification technologies have been mentioned to be suitable for H_2 production (Binder et al., 2018). Mainly, the DFB technology was developed to commercial scale for biomass steam gasification in a plant in Güssing, Austria (Pfeifer et al., 2009). So far, SEG was able to produce H_2 contents around 73% v/v higher than those of DFB, though, only pilot-scale installations have shown successful operation (Binder et al., 2018).

Table 2: Main biomass gasification technologies for bio-H_2 production.

Gasification Technology	Main Characteristics
Dual Fluidized Bed (DFB) Gasification (Pfeifer et al., 2009)	Gasification combined with combustion
	Bubbling fluidized bed gasification operates with steam, in absence of oxygen
	Combustion reactor works with air as a fast fluidized bed
	Heat is transferred from the combustor by circulating bed material
MILENA gasification technology (Van der Meijden, 2010)	Two fluidized beds like DFB
	Fast fluidized bed gasification operates with steam
	Combustion reactor works as a bubbling fluidized bed
Heat-pipe Reformer (Karl, 2014)	Combustion and gasification reactors are bubbling fluidized beds
	The gasifier is a pressurized vessel (2-10 bar) and operates at 800 °C
	Heat transfer from combustion to gasification is attained through heat pipes
Sorption Enhanced Gasification (SEG) (Parvez et al., 2021)	Two fluidized beds and a circulating loop of bed material are used
	$CaCO_3$ is used as bed material, which is converted into CaO in the combustor
	and moved to the gasifier where it absorbs CO_2 and originates $CaCO_3$

In Figure 1 are presented the most important operations to convert syngas into bio-H_2. Gasification gas composition depends on the gasification technology and conditions employed, and also on feedstock type. It should be as near as possible to the requirements of syngas utilisation to simplify cleaning and conditioning processes, to decrease CAPEX (capital expenditure) and OPEX (operational expenditure). However, syngas cleaning and conditioning procedures are of most importance, especially when poor quality feedstocks are used, to remove minor undesirable compounds and to increase bio-H_2 content. Two options are available: i) hot gas conditioning, where syngas is kept at high temperature, like hot cyclones, physical filtration at hot conditions, adsorption at high temperature, thermal cracking or thermal catalytic cracking processes, or ii) cold gas conditioning that uses syngas at low temperature (close to ambient temperature) and two options may be selected here: dry scrubbing or wet scrubbing. Examples of the former are cyclones, rotating particle separators, electrostatic precipitators, bag filters, baffle filters, ceramic filters, fabric/tube filters, sand bed filters, adsorbers,

etc., while for wet scrubbing may be used spray towers, packed columns, wash tower scrubbers, impingement scrubbers, venture scrubbers, wet electrostatic precipitators, wet cyclone sand, etc. (Costa et al., 2021).

Cold syngas cleaning operations are an option when syngas is used at atmospheric pressure and at low temperature. Normally, after the cyclone, the syngas goes into cooling or washing towers to collect tars. If syngas processing requires high temperature, hot gas cleaning processes are the best option to achieve good energy management and to lower operating costs. The selection of the most suitable process depends on syngas initial composition, purity required by syngas application, temperature and pressure of the gas utilisation technologies, complexity of these processes and degradation, losses and cost of the solvents or catalysts used in syngas cleaning. A very important issue in the selection of cleaning and conditioning processes is the temperature at which the syngas is going to be used.
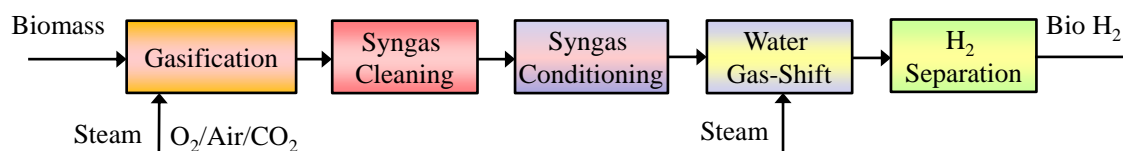

Figure 1: General layout of biomass gasification to produce Bio-H_2.

Next, the most significant processes for bio-H_2 production via biomass gasification, as illustrated in Figure 1, are reviewed in a summary form. First, the main syngas cleaning and conditioning processes (RME (rapeseed oil methyl ester) scrubber, amine scrubber for CO_2 removal, thermal catalytic cracking and syngas steam reforming) are revised.

RME scrubber for tar abatement is considered to be an important cold gas conditioning process in bio-H_2 production routes. In RME scrubber steam is condensed and tar removals from 5 to 1.5 g·m^{-3} were reported (Binder et al., 2018). No waste stream is discharged from the system, when emulsions are separated and burnt to provide energy. It was proven at the commercial scale in DFB plants in Austria (Güssing and Oberwart), Germany and in Sweden (Senden) (Binder et al., 2018).

Amine scrubber for CO_2 removal is also a cold gas conditioning process for bio-H_2 production routes. Meerman et al., 2013 tested different amines for CO_2 removal and the following order for CO_2 absorption capacity was reported: MDEA (methyldiethanolamine) < DEA (diethanolamine) < MEA (monoethanolamine) ~ aMDEA (activated MDEA with piperazine). However, some drawbacks still exist: a significant amount of energy is needed for the regeneration step, especially when H_2S is absorbed; some scrubbing liquid is lost by evaporation and has to be often refilled; corrosive behaviour of amines and the formation of non-soluble salts and foaming (Bauer et al., 2012).

Thermal catalytic cracking processes have been successfully reported for tar abatement for hot syngas cleaning and conditioning and different types of catalysts and conditions have been tested. There is much information about this subject in the literature, for instance Din and Zainal, 2017 reviewed catalysts for tar cracking and reported that there are still some challenges like catalysts deactivation, due to poisoning, erosion, attrition (dolomite), fouling, thermal degradation and phase transformation. Ni based catalysts were reported to be a good option for tar reduction.

Syngas steam reforming reactions to convert hydrocarbons (mainly CH_4) to increase H_2 formation have been widely studied by several authors. For example Tan et al., 2020 analysed the cross effect of several parameters such as: the type of hydrocarbon, catalyst type, temperature and the steam/carbon ratio, to achieve the best performance and maximize H_2 production.

The Water gas shift (WGS) reaction ($CO+H_2O \leftrightarrows CO_2+H_2$) is also crucial to increase bio-H_2 content in syngas while simultaneously decreasing the CO content. Two different types of catalysts may be used: low temperature catalysts (~200-350 °C) and high temperature catalysts (350-550 °C). Co-Mo-based catalysts are resistant to sulphur poisoning, while Zn-based catalysts are very sensitive to sulphur, both are examples of low temperature catalysts. An example of high temperature catalysts are Fe-Cr-based, which has shown to be relatively inexpensive, resistant to sintering (due to Cr_2O_3) and resistant to sulphur and chlorine compounds.

Main H_2 separation/purification technologies are pressure swing adsorption (PSA) and gas permeation through membranes. The later also operates in a continuous mode and is easily controlled. Different types of membranes for H_2 separation have been used: polymeric, porous (ceramic, carbon, metal), dense metal and ion-conductive membranes. Polymeric membranes have been significantly commercialized. However, the main challenge is to increase H_2 separation, as large selectivity has been reported.

H_2 purification could be increased by multistage membrane systems with recirculation of the permeate or retentate streams, but the improvement has to be enough to balance the rise in investment and running costs and this still needs to be demonstrated on a large scale (Pinto et al., 2013).

PSA is a cyclic adsorption process with multiple fixed beds, alternating between adsorption, where the adsorbent selectively retains the heavier components contained in the feed stream, and regeneration, where these same species are removed from the adsorbent (e.g. through the reduction of the total bed pressure). PSA is used in industrial hydrogen purification, producing H_2 with a purity greater than 99.99% (Voldsund et al., 2016). Besides being widely used at industrial scale, some new PSA developments have been reported, for instance, Streb et al., 2019 developed a new PSA/VSA (vacuum swing adsorption) process for co-production of CO_2 and H_2, after steam reforming and WGS, with the ability to obtain both components with a purity greater than 95% and recovery greater than 90%. PSA was tested in a DFB biomass steam gasification plant in Oberwart, Austria, where four vessels filled with activated carbon (Norit, RB2), as adsorption agent, and operating in a cyclic sequence led to high H_2 purity (99.97 vol % db) and H_2 recovery of 80-90% (Fail et al., 2014).

3. Bio-H_2 production routes from biomass gasification

Binder et al., 2018 did some process simulation calculations, using a steady-state simulation tool, and proposed two routes for bio-H_2 production via biomass gasification, one using DFB gasification and another one SEG technology. For both routes, steam is used for gasification, while air is used for the combustion reactor, which has the advantage of no pure oxygen needed. In Figure 2 is presented a general layout of biomass DFB gasification to produce bio-H_2. After DFB gasification and before the WGS reactor, it is advisable to have syngas cleaning and conditioning operations, depending on the feedstock type and on syngas initial composition, to prevent WGS catalyst deactivation and to increase its lifetime. However, if in the WGS operation, a catalyst resistant to sulphur is used, a detached process step for sulphur removal may not be necessary, as most of the organic sulphur compounds are hydrated in the WGS unit and converted to H_2S, which may be separated from the gas stream in the downstream amine scrubber. Some remaining organic sulphur is separated in the PSA unit and goes into the adsorbate flow (Binder et al., 2018). As tar abatement happens only in the RME scrubber, care should be taken about the amount of tar that may go into the WGS reactor, to ensure its operations in the right conditions and to prevent catalyst deactivation.
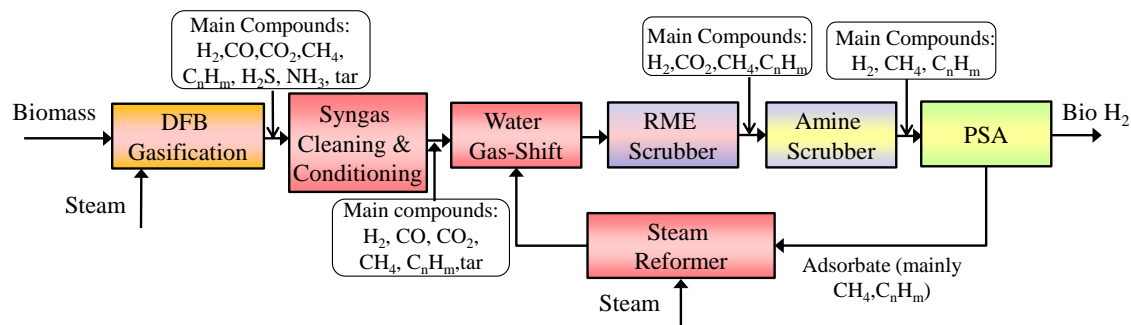

Figure 2: General layout of biomass DFB gasification to produce bio-H_2 (adapted from Binder et al., 2018).

After the WGS reactor, syngas goes into an RME scrubber for tar abatement, where steam is condensed, and next it goes to the amine scrubber, using aMDEA, to remove CO_2. After the amine scrubber, the gas is compressed and goes into the PSA. Further CO_2 removal happens in the PSA unit together with other compounds of the adsorbate. The PSA may use activated carbon as adsorbent and operating pressure may be around 10 bar. Pressurised H_2 recovery of about 85% and with purity of 99.97% were reported by Binder et al., 2018.

The adsorbate, containing mainly CH_4, C_2H_4, C_2H_6, H_2O, CO, CO_2 and H_2, is introduced in a steam reformer reactor to convert the hydrocarbons into CO, CO_2 and H_2. Afterwards, this stream goes into the WGS operation for further production of H_2. Some adsorbate may be burnt to supply the energy needed by the steam reformer. H_2 production via biomass SEG, shown in Figure 3, has fewer operations than Figure 2 route, because CO_2 is separated inside the gasifier by limestone. Thus, syngas is enriched in H_2 and the WGS reactor may not be needed. The RME scrubber for tar abatement is used and afterwards, syngas is compressed before going to the PSA unit. As the PSA adsorbate is rich in CH_4, this stream may go to a steam reformer to increase H_2 formation. As mentioned for the DFB gasification layout, part of the adsorbate may be used to produce energy for the steam reformer.

The main drawback of this SEG layout is the TRL (Technology Readiness Levels), which is lower than that of DFB gasification. Although SEG pilot-scale experiments have shown good results and operation, demonstration scale operation is still needed. The overall process chain of DFB has also a higher TRL than the SEG route.
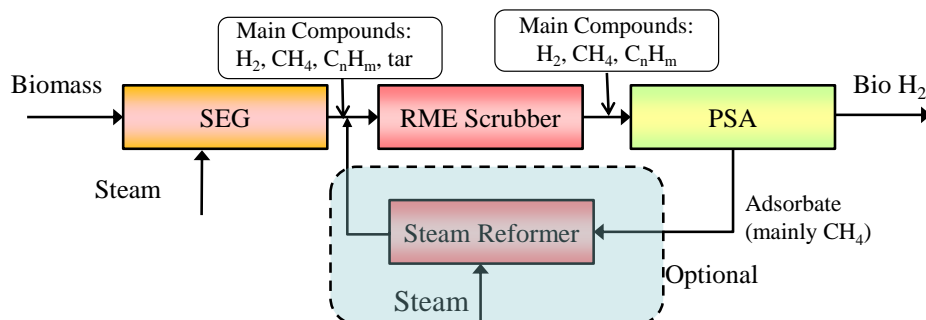

Figure 3: General layout of biomass SEG gasification to produce bio-H_2.

Other bio-H_2 production routes from biomass gasification may be found suitable, though the TRL of some of the technologies are nowadays lower than those of previous routes. In Figure 4 is presented a concept based on hot gas conditioning. If DFB gasifier is not used, an oxygen stream will be needed. Thermal catalytic processes are used for gas cleaning and conditioning steps for tar abatement and nitrogen, sulphur and chlorine compounds removal. Different types of catalysts and sorbents may be used and in literature, there is much information about this subject (e.g., Din and Zainal, 2017). The number of operations depends on initial synthesis gas composition, the catalysts and conditions used in each process, and the specific requirements demanded by the catalyst used in the next operation. It needs to be kept to a minimum to decrease syngas thermal loss and reduce CAPEX and OPEX. Next, the steam reforming unit is important to convert hydrocarbons into H_2, CO_2 and CO. Further production of H_2 is obtained in the WGS reactor. The product gas stream main content is H_2 and CO_2, with some contents of hydrocarbons and CO. After that, the gas is cooled down and compressed if it is introduced into a PSA unit. H_2 could be separated by membranes instead of PSA, as syngas is at high temperature at this stage. Membranes usually work at lower pressure, but at higher temperatures; however, membranes TRL is lower. Marcantonio et al., 2019 compared PSA and palladium membrane performance and reported that hydrogen recovery ratio was around 28.9% higher for the palladium membrane in relation to the PSA configuration, though PSA economic viability was higher.
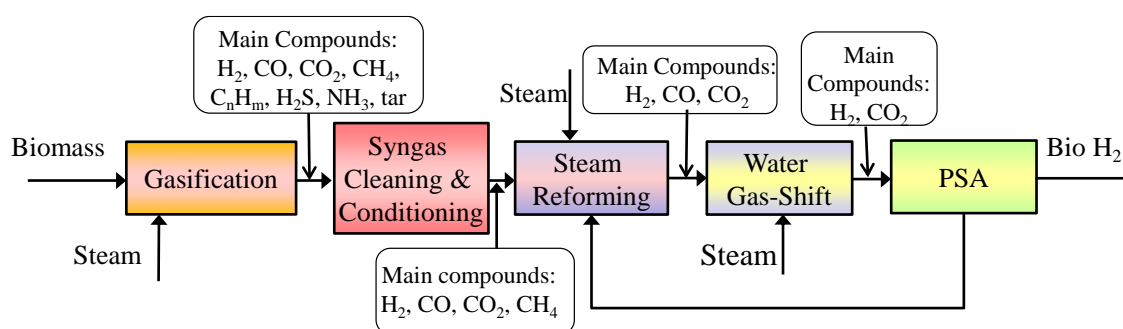

Figure 4: General layout of concept based on syngas hot gas conditioning to produce Bio-H_2.

Many researchers have been studying different processes to obtain bio-H_2 from biomass gasification, either using experimental installations or simulation studies, and have reported that biomass gasification is a good option to produce bio-H_2. In general, life cycle assessment and techno-economic analyses have shown encouraging results, though many variables may compromise the overall viability of bio-H_2 production via gasification. So far, the routes presented in Figure 2 and 3 seem to be more feasible, especially the DFB route, due to the higher TRL. However, these promising process routes have not yet been fully tested at demonstration scale and there are still some drawbacks and technological challenges that need to be overcome to increase the overall feasibility. Thus, political support and financial incentives are needed for the implementation of H_2 production through biomass gasification.

4. Conclusions

Bio-H$_2$ will be an important renewable secondary energy carrier in the near future and biomass/wastes gasification is a good option to produce it, being an alternative for future decarbonisation applications. Although some technologies are proven and available on the market for similar applications, namely syngas cleaning and conditioning, WGS, scrubbers and PSA units, there are still some drawbacks and technological challenges that need to be overcome to improve the overall bio-H$_2$ production feasibility.

Bio-H$_2$ production route from biomass gasification depends on biomass type and composition, as it will affect syngas cleaning and upgrading. SEG and DFB gasification are good options for H$_2$ production. SEG needs less operations than DFB, however SEG challenges are higher as SEG TRL is lower than DFB TRL.

Demonstration of the full process chain for bio-H$_2$ production from biomass gasification is still needed, especially for SEG. Thus, governmental support and subsidies will probably be necessary for the implementation of bio-H$_2$ production from biomass gasification to reach stable operation to market maturity.

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