Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Information to

Perspective on the hydrogen economy as a pathway to reach net-zero CO_2 emissions in Europe

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Additional material for section 3.3: Low carbon hydrogen production from fossil fuels

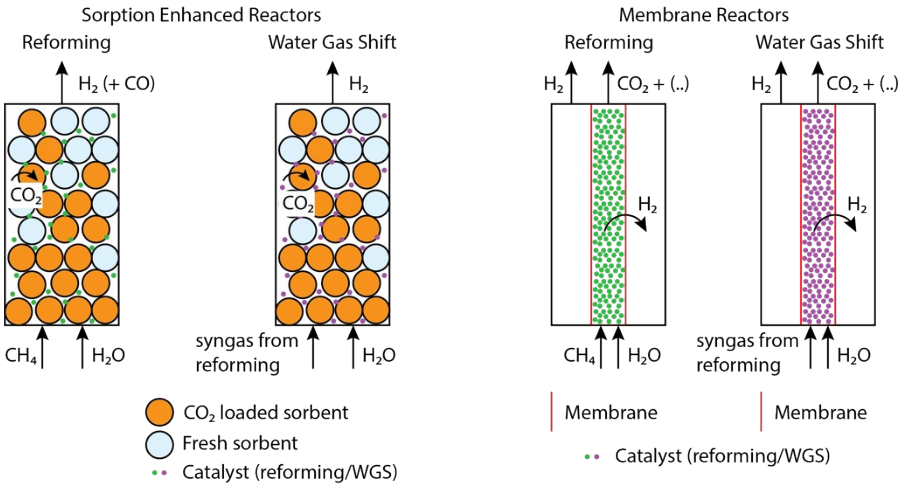

Figure 1. Conceptual overview of novel integrated concepts. left: sorption enhanced reactors; right: membrane reactors. Multiple reactor configurations exist for each process, e.g., fixed or fluidized beds.

H2 production technologies that exploit Le Chatelier's principle:

SEWGS. The technology has been tested and demonstrated in industrially relevant conditions and has shown high performance under different operating regimes and syngas types.[1–4] A next step is to demonstrate a *multi* column SEWGS cycle under real working conditions before the step to commercialization can be made. While the process has shown promising energy and cost performance, it suffers from low hydrogen purity, as only acid gases are retained by the sorbent (hydrotalcites). This implies that N2, Ar, CO and CH4 in the entering syngas typically end up with the hydrogen product. Therefore, SEWGS is particularly attractive for those processes where hydrogen purity need not be very high, e.g., combustion or ammonia synthesis. Alternatively, a hydrogen purification unit must be installed downstream of the SEWGS.

SER: Similarly to SEWGS, SER allows for improvements in i) the energy efficiency, with a natural-gas-to-hydrogen ratio 3-6 percentage points higher than a fired tubular reformer (FTR) used in the SMR process; in ii) the carbon-capture ratio, with 99% capture compared to 85% in FTR;[5] and iii) a potential reduction in costs, with reduced costs for H_2 production and CO_2 capture (8% and 52%, respectively).[6] As with SEWGS, in the case of SER, high H_2 purities require the adoption of an additional PSA hydrogen purification unit.

Membrane reactors. Similar to the sorption-enhanced case, the main advantage lies in overcoming the thermodynamic limits for conversion of CH_4 or CO compared to conventional reactors, and in the possible reduction in reactor numbers and plant complexity. While a wide variety of membrane materials can be selected, for hydrogen production Pd and Pd-alloys (e.g. Pd-Ag, Pd-Cu) are the most studied, where the active layer is typically deposited on a ceramic support. Different reactor configurations have been proposed in literature including packed-bed membrane reactors (PBMR), fluidized-bed membrane reactors (FBMR) and micro-membrane reacors (MMR). While PBMR is the most studied membrane reactor configuration, recent findings show that the industrial application will most likely use FBMR, where mass-transfer limits are less critical.[7] PEM fuel-cell-compatible hydrogen purity can be reached in membrane reactors, however, additional units are needed to increase H_2 recovery and/or CO_2 purity. For the former, a PSA unit for hydrogen recovery from the membrane retantate can achieve an overarching H_2 recovery of 80-90% for purities above 99.999%.[8] For the latter, a CO_2 cryogenic can achieve storage purity (>95%) while also recovering hydrogen (along with other impurities).[9] Concluding, in order to reach industrial deployment of membrane reactors at scale , a number of issues need further advancment: (i) cheaper materials compared to those in Pd-based reactors, (ii) cost reductions in modules fabrication, (iii) higher stability under operating conditions in harsh environmnets, e.g., at high temperatures, and (iv) better robustness to aging and poisoning.[10,11]

Chemical looping and methane deposition. In the first case, chemical looping, which builds upon repetitively reducing and oxidizing a metal oxide in suitable reactors, is adopted to produce hydrogen (in place of heat as in conventional chemical-looping combustion schemes). In the second case, also known as methane cracking, methane thermally decomposes to solid carbon and gaseous hydrogen in presence of a suitable catalyst.

Additional material for section 3.3: Hydrogen production from biogenic sources

Entrained-flow gasification at high temperature in presence of oxygen. Entrained-flow gasifiers (Figure 2) are proven technology for coal gasification,[12] but scale up for wood gasification has so far proven difficult, not in the least because scale-up beyond lab pilot stage requires large equipment and equivalently expensive investments. Entrained-flow gasification operates at high temperatures, usually between 1300 and 1500°C, and at high pressure (25-30 bar). The reactors are most commonly oxygen blown and, therefore, require an air separation unit (ASU) or other oxygen source.[13] The main advantage of high-temperature gasification is the virtual absence of tars in the syngas, but the high temperature and pressure require expensive reactors, including a refractory lining in the gasifier that needs frequent replacement during the reactor lifetime.[13] When produced at large scale, however, high-temperature gasifier trains have a lower capital-cost footprint than low-temperature trains, because they benefit more from economies of scale.[13] Another drawback of high-temperature gasification is the high sensible heat content of the syngas, and the inherently lower cold-gas efficiency (biomass energy to cold syngas energy efficiency) compared to low-temperature gasifiers, loosing much exergy in the syngas cooler.[12]

The fuel flexibility of a single gasifier is typically low as it needs careful design to the supplied feedstock. It needs mostly torrefied wood (to increase bulk density and reduce moisture content) at very small particle sizes of 0.1-1 mm and moisture content below 15%.[13] This implies that its feedstock needs to be dedicated biomass from production forests or its residues, placing limits on practical implementation, as dedicated wood production for energy purposes may face societal resistance. As said before, scale-up of this technology is another major hurdle, both in terms of investment and performance, and the initial optimism on high-temperature biomass gasification has faded due to slow progress. If scalable, and in the scope of hydrogen production, biomass gasification could make use of synergies with large-scale water electrolysis, where the electrolyser provides the oxygen to the gasifier, and expensive and energy intensive equipment like ASUs might be eliminated.

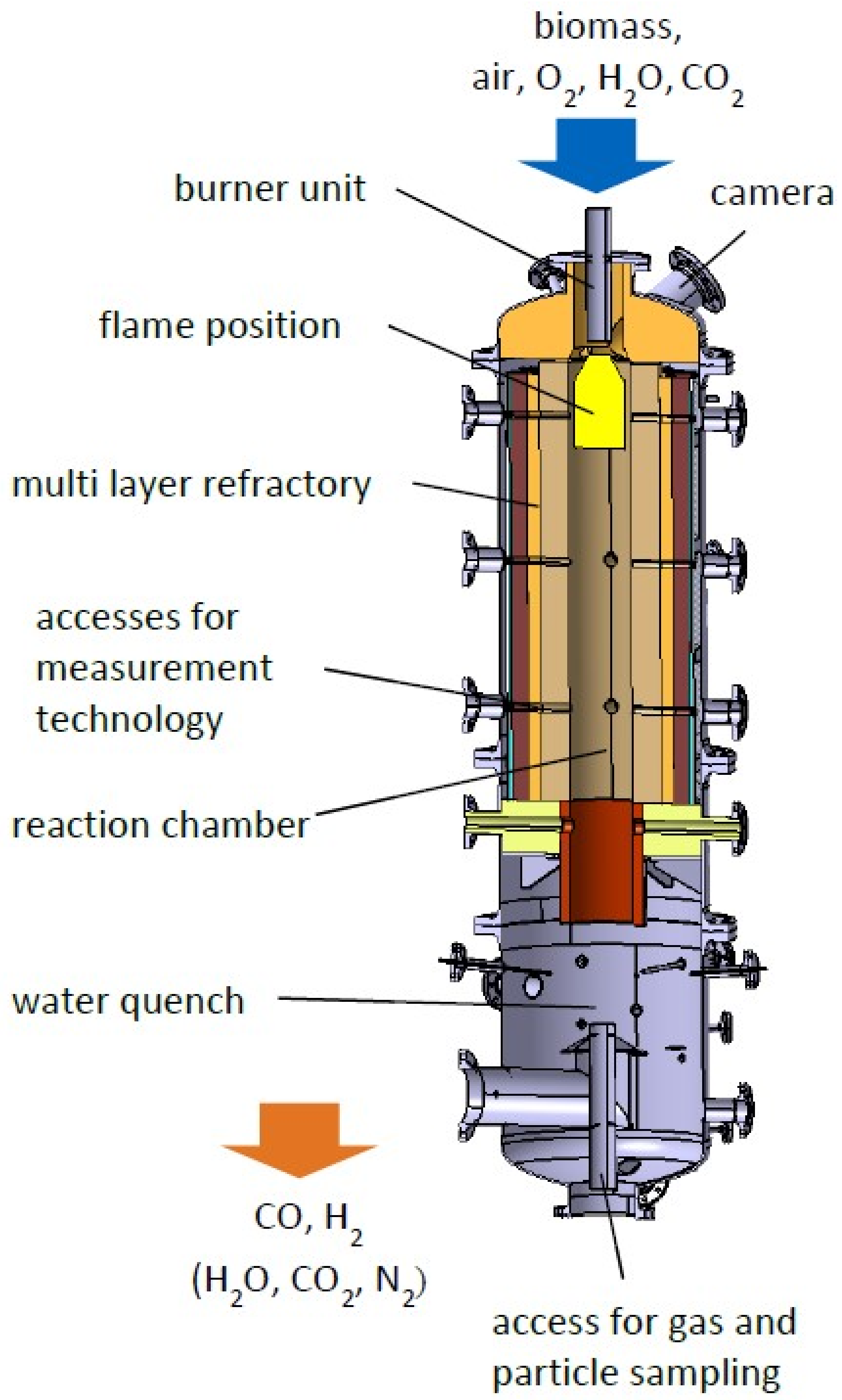

Figure 2. Schematic representation of an experimental entrained-flow gasifier.[14]

Low temperature biomass gasification in dual fluidised beds. Fluidised-bed gasifiers (*Figure 3*) are deemed most suitable for steam gasification at lower temperature because of their high hydrogen yields and relatively low tar formation,[15] the latter being a notorious problem for downstream gas cleaning due to tar's condensation at reduced temperatures. A key difference of low, compared to high, temperature gasifiers is their product gas, which includes, besides syngas and tars, notably methane (and other alkanes) and chars. Existing, built, large-scale Dual Fluidised Bed gasifiers include the 40 MW_{th} Silvagas plant in the USA and the 32MW_{th} GoBiGas plant in Sweden with commercial units being sold by market parties,[16] although these plants are still an order of magnitude smaller than what might be expected of commercial-scale hydrogen plants and the question is if the fluidised beds can be scaled enough to truly benefit from economies of scale.

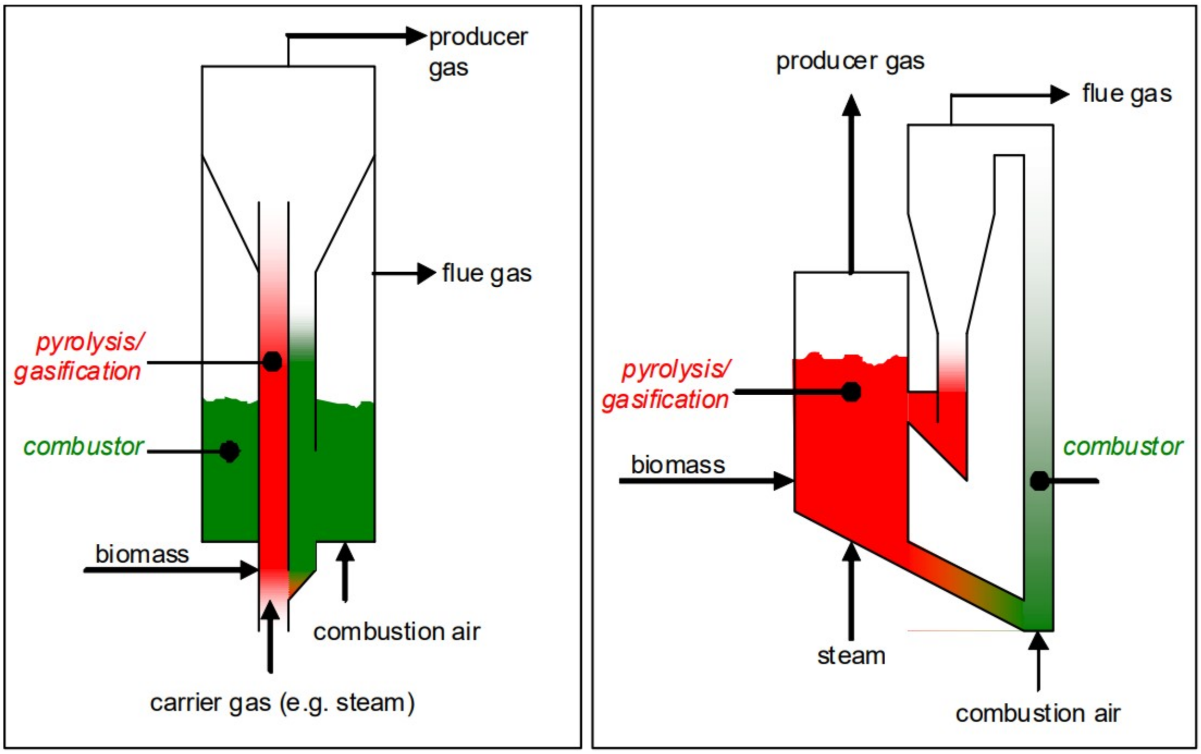

Figure 3. Comparison of two dual fluidised-bed gasifier types. The ECN Milena gasifier (l) and the Güssing FICFB gasifier (r).[17]

The fuel flexibility of fluidised-bed gasifiers is higher than that of entrained-flow gasifiers, but they co-produce methane and tars. The tar-cracking performance is one of the major challenges for gasifier designs, because total elimination requires temperatures over 1250°C.[15] A longer residence time in the gasification section can, however, reduce the amount of tars in the product gas, and this is one strategy often applied to address this problem, also, downdraft gasification can help in this respect. Char conversion is typically the rate-limiting step and incomplete, leaving char to remain in the product gas, whereas gas/liquid oxidation and reforming rates are much higher.[15]

The addition of catalysts to the bed material can increase the hydrogen yield and/or selectivity and can reduce the formation of tar. The issue of tar formation can also be addressed post the gasifier, using a catalytic post-reformer or tar cracker, plasma cracking, or an oil-based gas washer (e.g., the OLGA technology developed by the Energy Research Centre of The Netherlands).[18] However, if the purpose of the plant is maximisation of hydrogen yield, then using a tar cracker is arguably the most sensible option, since the methane produced in the product gas will also be reformed to syngas at cracking conditions.

In terms of scale-up, system improvement and commercialisation, the search is for systems that can handle biomass types of varying composition, particle size and moisture content without causing operational issues.[15] This would have great benefits as more waste biomass streams can be used, potentially reducing some of the concerns of dedicated bioenergy crop use for energy production.

Advanced technologies for biomass gasification. One potential advanced biomass gasification technology, that may also circumvent some of the issues of entrained-flow gasification, is TRIG (Transport Integrated Gasification, Figure 4), developed by KBR.[19] TRIG is an oxygen-blown steam gasifier that operates at just above 1000°C and at 45 bars of pressure,[20] placing it in-between low- and high-temperature gasification. It was designed for gasification of low-rank coals, i.e., coals containing high moisture and ash levels, applying high solids circulation rates to create a highly turbulent environment, improving gas-solids contact and thereby heat and mass transfer rates.[19,21] Ash is separated in a disengager and subsequent cyclone and flows down into a standpipe, leaving the standpipe at the bottom as a coarse ash. This type of gasifier may be very useful for biomass gasification, which also contains a high amount of ash and moisture. The benefit over entrained flow is that the lower temperatures keep the ash in the solid phase and allow easier handling of large ash volumes (compared to, e.g., slag formation), plus leading to higher cold-gas efficiencies. TRIG has so far been tested only with biomass co-gasification but showed good results up to 30%-wt biomass feed.[20]

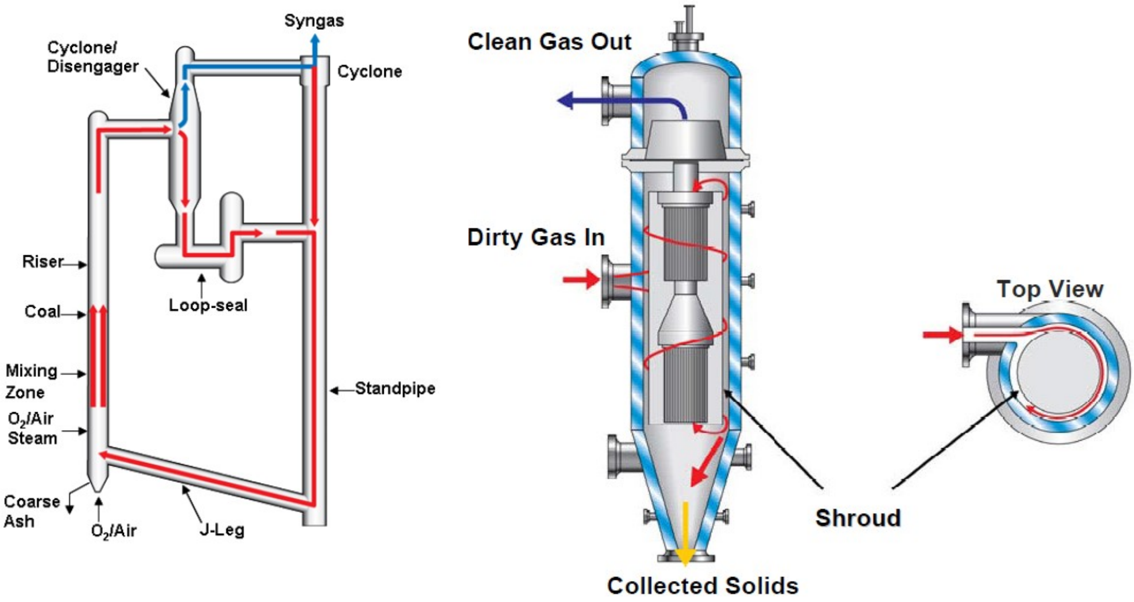

Figure 4. Schematic representation of the TRIG gasifier (l) and the TRIG particulate control device.[19]

Another technology relevant in the context of hydrogen production through biomass gasification is calcium or chemical-looping gasification (Figure 5). In this concept, CO_2 is removed already inside the gasifier (see also Section 3.3), so that expensive downstream CO_2 removal equipment is no longer needed.[22,23] Calcium and chemical-looping gasification add metal or calcium oxides to the gasification bed, that selectively adsorb the CO_2. Calcium oxide has the additional benefit that it acts as a tar cracker, thereby allowing the integration of three separate process steps (gasification, CO_2 separation and water gas-shift). Also, the selective adsorption of CO_2 shifts the reaction equilibrium to the production of more hydrogen, improving yield and heating value of the product gas. The calcium and metal carbonates are regenerated in the fuel reactor of the dual fluidised bed, producing a stream of pure CO_2 when regenerated in oxygen, using the char produced in the gasification reactors as fuel.[23]

Adanez et al.,[24] mention significant challenges that prohibit the one-to-one use of well-established coal looping systems for biomass. First, the volume of volatiles released by biomass is larger than for coal, impeding the decomposition of solids, leading to lower syngas yields when residence time and fluidisation are left unadjusted. Also, biomass char is more reactive than coal char, requiring further adjustment of residence time, fluidisation and ratios of fed fluidisation agents. Third, the biomass ash composition is also different, potentially leading to higher corrosion rates inside the equipment.

However, in general, calcium and/or chemical-looping reforming of biomass seem promising strategies for highly integrated and efficient biomass-based hydrogen production.

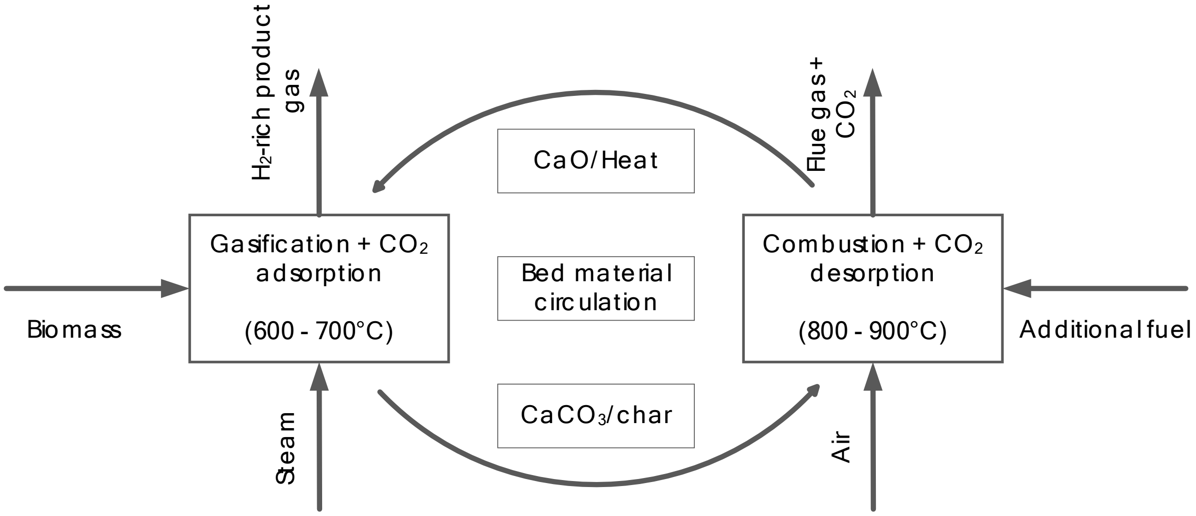

Figure 5. Schematic representation of biomass calcium looping gasification, based on Hanak et al.[25] *Note that in this scheme the calcination reactor is air blown. If an oxygen-blown reactor would be deployed, an easy-to-separate* CO_2*/water mixture would be produced, facilitating easy* CO_2 *separation for permanent storage.*

Syngas and product gas processing systems. Since biomass is a biogenic feedstock, it contains many chemical elements that need removal to produce pure hydrogen. They include chlorine (in the form of HCl), sulphur (H_2S and COS), nitrogen (NH_3 and HCN), ash, char and tar.[16] The exact composition heavily depends on gasification technology and feedstock used and therefore, often, the downstream gas-cleaning train is designed in conjunction with the gasifier. Most of the clean-up technologies are commercially available, and therefore do not present the largest upscaling risk, although they add cost and complexity to commercial biomass gasification plants.

The gas cleaning train of entrained flow biomass gasifiers is very similar to that of entrained flow coal gasifiers [12,26]. After the gasifier, the hot syngas first needs to pass through a quench: the temperature is so high that otherwise fly ash remains in a liquid state and deposits on the downstream gas cooler tubes. It is then led through a high efficiency gas cooler, cooling down to ~ 200°C, that aims to recuperate the majority of the sensible heat left in the quenched syngas. The cooled syngas is afterwards cleaned from remaining particulates, chlorine and ammonia in a water scrubber. Typically guard beds are used to remove COS and heavy metals. The removal of sulphur can be done pre or post the water gas-shift (WGS), where often the choice is made to allow for a sour-WGS, only removing the H_2S after the shift. This is done simultaneously with the produced CO_2, using, well known technologies as Selexol or Rectisol and sparing one separation step. To maximise hydrogen production, an additional, final, shift can be needed, followed by hydrogen purification in a pressure swing adsorption (PSA) unit [12,26].

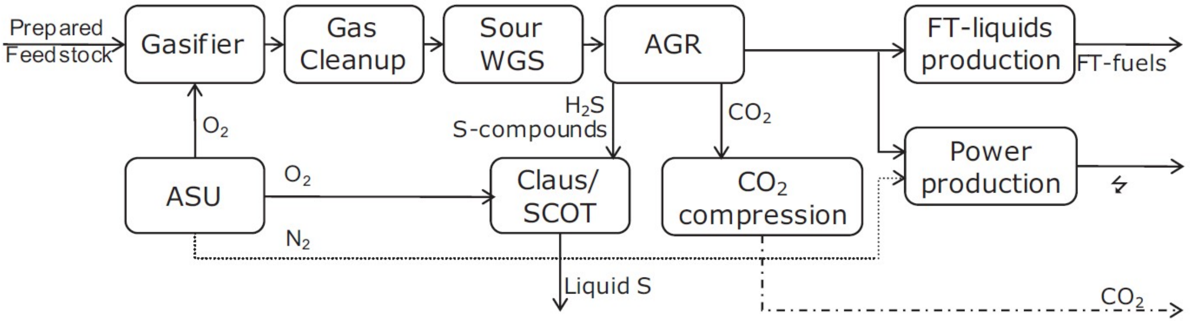

Figure 6. Process flow diagram of the entrained flow gas cleanup train presented in [26]*. In this line up, the produced syngas is used to produce FT liquids and power.*

Van der Roest et al. [16], presented the full gasification and gas cleaning train for the Milena dual fluidised bed gasifier, developed by the Energy Research Centre of The Netherlands [27] and afterwards commercialised by Royal Dahlman. It includes a cyclone to remove char and ash at elevated temperature of 400°C, to avoid tar condensation. The tar itself is removed by the proprietary OLGA technology, an oil scrubbing technology in which tars selectively dissolve. It is then followed by a water scrubber to remove part of the hydrochloride and ammonia, after which the product gas is compressed and fed to a catalytic hydrodesulphurisation (HDS) reactor at 3 bar and 350°C. In the HDS, organic sulphur compounds are converted to H_2S, hydrogen cyanide is converted to ammonia, and the aliphatic olefins are hydrogenated. Finally, a zinc oxide bed converts all hydrogen sulphide into zinc sulphide, leaving the gas essentially free of sulphur. Full mass and energy balances of the Milena and gas processing train are provided in the supplementary materials of ref [16]. Van der Roest et al., assumed the resulting clean product gas to be fed to a solid oxide fuel cell able to convert methane and CO. If the purpose is hydrogen production, an additional WGS step (e.g., [18]) and further methane removal (e.g., by (V)PSA) would be required.

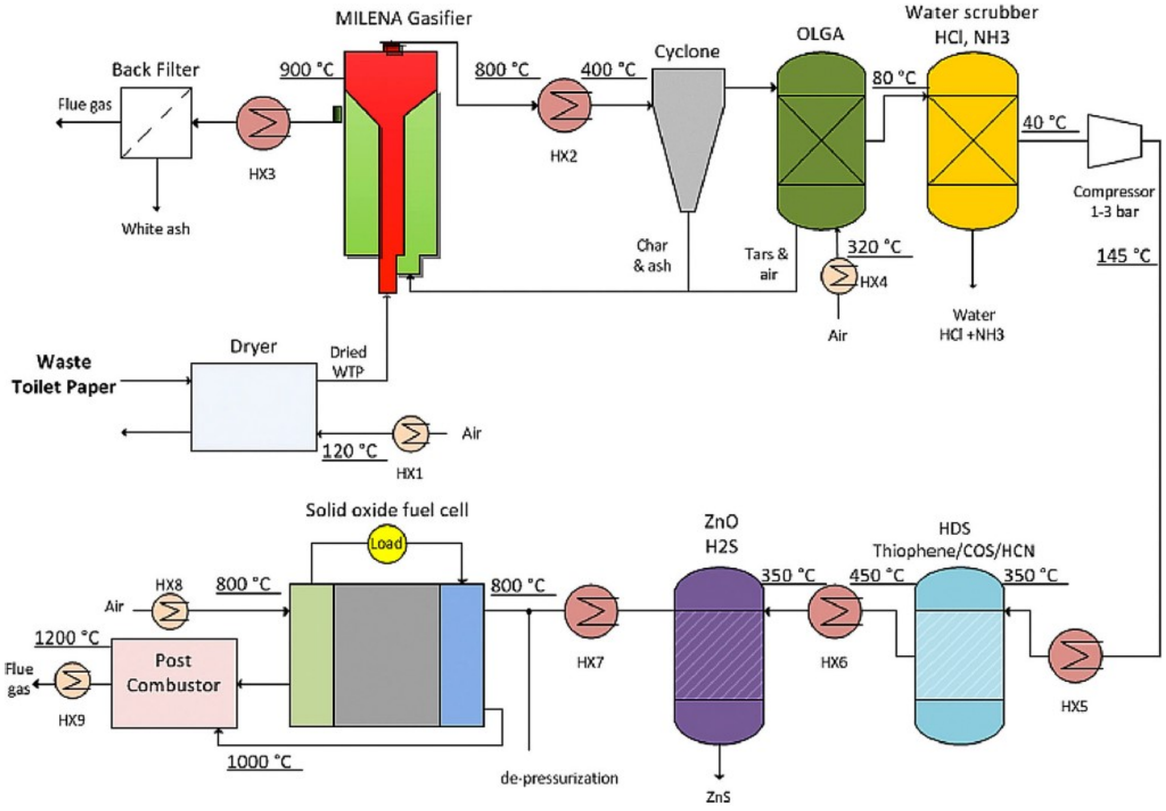

Figure 7. Process flow diagram of the gas cleanup train for fluidised bed gasifiers in [16]*, here applied to the ECN Milena gasifier and using the cleaned product gas in a fuel cell for electricity production.*

The TRIG gasifier uses a cleaning train very similar to that of an EF gasifier, including syngas cooler, particulate control (Figure 4), and scrubber to remove chlorine and ammonia before entering the sour water-gas shift [20]. An acid gas removal unit then removes sulphur, reactive nitrogen and CO_2. Rectisol was selected by Larson et al. [20] for very deep contaminant cleaning, however, the still present tars provide an issue here as tars easily dissolve and accumulate in methanol. Therefore, a prewash was installed, which would not be necessary for normal entrained flow gasifiers. Finally, a ZnO bed is used to remove any trace contaminants from the syngas. Also here, to maximize hydrogen production, a second shift can be installed, after which the hydrogen may be purified in a PSA.

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