

# Production of Biohydrogen from gasification of waste fuels: pilot plant results and deployment prospects

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## Abstract

*Hydrogen is seen as a key element of the future energy mix because it does not generate greenhouse gas emissions at the point of use. Understanding the technologies that can generate low carbon hydrogen is essential in planning the development of future gas networks and energy generation via fuel cells. One promising approach is hydrogen production by gasification of waste, referred to as biohydrogen. This paper summarises work undertaken to design a commercial Waste-to-Hydrogen (WtH<sub>2</sub>) plant, which includes an assessment of future markets for hydrogen, the identification of an appropriate scale for the plants, and development of specifications for process design and output streams. An experimental programme was undertaken to demonstrate bioH<sub>2</sub> production from refuse derived fuel (RDF) at pilot scale and provided experimental data to underpin commercial designs. On this basis, a reference design for small commercial plants was developed for bioH<sub>2</sub> production for heating and transport utilisation. A preliminary carbon assessment shows that carbon savings for*

*biohydrogen in a commercial scale are more than four times greater than alternative technologies.*

**Keywords:** Biohydrogen, Waste Gasification; Waste-to-Hydrogen; Biofuels

## 1. Introduction

In recent years hydrogen has received increasing attention as a potential fuel that could be produced from non-fossil fuel sources (Hart *et al.*, 2015; Barisano *et al.*, 2017; Ogden, 2018), both because it can be generated with low greenhouse-gas (GHG) emissions, and because it generates no emissions at the point of use. Hydrogen is being promoted as an ideal energy vector for heating and transport; assuming that storage and distribution will no longer be an issue in the near future, the outstanding question is how to produce hydrogen with the minimum carbon impact (Balcombe *et al.*, 2018). There are currently two prominent pathways for the production of low carbon hydrogen: one is through reformation of natural gas (by Steam methane reforming (SMR) or Auto-Thermal Reforming (ATR)), combined with carbon capture and storage (CCS). The other one is water electrolysis utilising electricity from renewable sources (e.g. wind and solar).

Steam and autothermal methane reforming involves reacting natural gas with steam or limited amount of oxygen, at high temperatures over a catalyst to produce syngas (a mixture of hydrogen and carbon monoxide). This is then further processed to maximise H<sub>2</sub> generation (via water gas shift reaction) and separate H<sub>2</sub> product from a CO<sub>2</sub>-rich stream (Iulianelli *et al.*, 2016). Production capacities of hydrogen from a typical steam methane reforming plant range between 150 and 440 MW with an energy efficiency of typically 70% (Ogden, 2018). Traditionally, a major part of the hydrogen consumption in oil and gas refineries is covered by

hydrogen produced as a by-product from other refinery processes or from SMR, which also represent a major source of carbon released into the atmosphere from petroleum industries (Al-Salem, 2015). If SMR is to become a major low-carbon source of hydrogen, carbon capture and storage is essential. It is estimated that between 71% and 92% of the CO<sub>2</sub> in steam methane reforming can be captured (Rubin *et al.*, 2012); however higher capture rates will be needed if the process is to be used in the long term. Furthermore, CCS barriers are not exclusively technical, with CCS cost being the most significant hurdle in the short to medium term (Budinis *et al.*, 2018). Among the new developments to produce low carbon hydrogen from methane is the sorption-enhanced SMR, which combines steam-reforming of methane and CO<sub>2</sub> absorption together in a single step. This configuration has two major advantages: on the one hand, the produced H<sub>2</sub> can have a purity of 98% with only a small amount (ppm level) of CO and CO<sub>2</sub> thus minimizing the requirement on purification (Di Giuliano *et al.*, 2018). On the other hand, the continuous removal of the produced CO<sub>2</sub> from the system by a solid absorbent pushes the reaction to completion, enhancing hydrogen yields significantly. SMR and sorption-enhanced H<sub>2</sub> production have been covered by a few excellent reviews (Barelli *et al.*, 2008; Shokrollahi *et al.*, 2016; Wu *et al.*, 2016; Di Giuliano *et al.*, 2018). The key challenge of the latter is the multicycle durability of CO<sub>2</sub> absorbent, which must be improved.

Water electrolysis also offers a small-scale solution that can be cost effective for some applications such as filling stations for hydrogen vehicles (Zeng and Zhang, 2010). However, currently the cost of hydrogen produced by electrolysis is far more expensive than SMR hydrogen (£6.20/kg versus £1.90/kg for transport-grade) and it does not offer significant greenhouse gas (GHG) benefits unless renewable electricity is used. Power-to-gas (PtG) technologies rely on this principle. This development is particularly attractive due to the

availability of renewable power generation in excess of immediate electricity demand and an expectation that this availability will increase with the share of intermittent renewable power generation (Götz *et al.*, 2016).

Several techniques have been proposed by many researchers for the thermal conversion of solid organic materials to hydrogen rich syngas, via gasification or pyrolysis (Siedlecki and de Jong, 2011; Bocci *et al.*, 2014; Miandad *et al.*, 2016; Al-Salem *et al.*, 2017; Barisano *et al.*, 2017). The hydrogen can then be separated and upgraded to a product referred to as biohydrogen (bioH<sub>2</sub>). Biohydrogen offers the prospect of low carbon hydrogen production from low-grade - in large fraction renewable – fuels, at parity with the cost of natural gas, and with the potential of negative carbon emissions if the separated CO<sub>2</sub> is sequestered (Zech *et al.*, 2015). A number of studies have been reported in the literature for biohydrogen production from first-generation biomasses, especially from starchy and sugar-rich biomasses due to easy fermentability attribute of these feedstocks by anaerobic organisms which increases H<sub>2</sub> yield compared to other organic substrates (Chong *et al.*, 2009; Argun *et al.*). The biggest obstacle when using these sources as feedstock is the utilization of land and clean water to produce energy crops instead of food production. Furthermore, there is a debate over the environmental impact of biofuels agriculture related to over-usage of water and fertilizers (Molino *et al.*, 2018).

Waste and second-generation biomass materials, although readily available and abundant, have limited uses in terms of chemical feedstocks, due to the need for pre-treatment and presence of many contaminants which add complexity and costs (Materazzi and Lettieri, 2017a). Thermochemical treatment of waste for hydrogen or chemical production, therefore, presents a number of unique issues demanding specific design choices and technical

solutions. Generally speaking, the conversion schemes use heat and various combinations of steam, oxygen and CO<sub>2</sub>, to convert the feedstock to various amounts of char, hydrocarbon gases, hydrogen, and carbon oxides, with ash being a by-product of most waste feedstocks (Basu, 2010). Ash residues are usually classified as a hazardous waste on account of their high alkalinity and other pollutant species (e.g. heavy metals and soluble chloride and sulphate salts); as such, they require specific treatment before disposal (Chang *et al.*, 2009). Therefore, before bioH<sub>2</sub> from waste can be deployed commercially several barriers must be overcome. Firstly, the technical feasibility of hydrogen production from waste derived feedstock must be demonstrated to show that the concept is credible. Secondly, the process must be optimised for commercial deployment, with designs produced, environmental impact understood and costs modelled. Finally, the chosen designs must be deployed at larger scale, with hydrogen supplied to end users. Extensive work is needed to push forward commercial deployment of hydrogen production from waste by systematically working to address each barrier.

This paper details the provisions taken to address these challenges and the reasoning behind them. In doing so it draws out some of the common challenges faced by the industry and the way in which the proposed approach, in particular how the syngas is produced, confers certain advantages when it comes to use of a syngas in a catalytic conversion process. Within this context, Section 2 summarises work undertaken to define a functional specification for a commercial Waste-to-Hydrogen (WtH<sub>2</sub>) plant, which includes an assessment of future markets for hydrogen, an appropriate scale for the plants, and development of specifications for output streams. Section 3 describes the experimental programme, which demonstrated bioH<sub>2</sub> production from waste at pilot scale and provided experimental data to underpin commercial designs. Section 4 summarises the reference design developed for commercial

bioH<sub>2</sub> production and discusses the drivers behind design choices. Future process improvements are also identified, along with an early stage assessment of carbon emissions.

## 2. Waste-to-Hydrogen plant: challenges and prospects

While biohydrogen production has traditionally focused on homogeneous biomass, more difficult feedstocks, such as municipal and other solid waste streams, could find application. The overall process presented in this work has focused on waste feedstocks, primarily municipal solid waste (MSW), as this represents the most technically challenging feedstock with the highest treatment costs, and will be the focus of early plants in the future. Feedstocks such as wood would require minimal process adjustments from conventional Biomass to Methanol (BtM) or Biomass to Liquids (BtL) plants, and have largely been discussed elsewhere (Bridgwater, 2003). This section provides an overview of the main transformation steps for production of bioH<sub>2</sub> from wastes. The specification for the baseline feedstock, scale of operation, and product use are discussed for the final plant design.

### 2.1 Hydrogen use and distribution

Hydrogen has been viewed as a potential vector to decarbonise transport for the last two decades. Currently electrification is seen as one of the prime pathway for decarbonisation of the passenger vehicle sector and is likely to see larger growth in the short term than adoption of hydrogen. Hydrogen fuels cell cars complement the advantages of electric vehicles by offering extended ranges and faster refuelling, and benefit from development of electric drivetrains, which are common to both (Granovskii *et al.*, 2006). While electrification looks set for a large role in decarbonising cars, there are fewer low carbon solutions for heavy goods vehicles (HGVs) and buses (Hua *et al.*, 2014). Electrification of HGVs is not feasible with

current battery technology and the charging time for electric buses is a substantial constraint on utilisation. Conversion to biomethane or bioSNG is also one solution (Zhang, 2010). Hydrogen, however, offers zero tailpipe emissions, particularly advantageous for urban environments and buses, which typically operate as back-to-base enabling gradual roll out of hydrogen refuelling infrastructure (Verhelst *et al.*, 2014).

Biohydrogen's potential as a gas for direct heating use is also gaining a considerable attention. Blending hydrogen and natural gas is already undertaken across Europe. In parts of Germany a blend of up to 10% by volume hydrogen in natural gas is permitted. In Holland, injection of hydrogen up to 20% by volume was trialled at Ameland (Kippers *et al.*, 2011). Currently the UK gas grid does not accept more than 0.1% hydrogen by volume (Hodges *et al.*, 2015). However, a site-specific exemption has been granted by the Health and Safety Executive (HSE) to blend hydrogen at 20% into the gas network at Keele University, and it is anticipated that blending of hydrogen from a variety of sources into the gas distribution could be feasible as early as 2020 (Hodges *et al.*, 2015). Injecting hydrogen into the network to create a blend for use by consumers provides an opportunity for the early roll out of biohydrogen production, since there is significant demand for low carbon replacements for natural gas that are compatible with existing appliances. Furthermore, shifting completely to hydrogen offers a longer-term opportunity for bioH<sub>2</sub> because it offers far greater carbon savings than SMR hydrogen. However, whilst the national transmission systems are capable of carrying much larger volumes of gas than the distribution networks, there are a number of risks and constraints relating to both the materials of construction and the nature of the gas consumers connected to it, which mean that there are barriers to accommodating hydrogen except in a blend, and at relatively low blending levels (Northern Gas Networks, 2016). These risk levels

are associated with introducing hydrogen blends into existing natural gas pipeline systems and do not apply to new pipelines dedicated specifically to hydrogen transportation, which are designed and managed differently from the existing natural gas pipeline installations (Witkowski *et al.*, 2018). Worldwide, there are already more than 4,500 km of hydrogen pipelines in total, the vast majority of which are operated by hydrogen producers. The longest pipelines are operated in the USA, followed by Belgium and Germany (HyARC, 2017).

## **2.2 Scale definition and feedstock preparation**

Compared to biomass, MSW materials introduce a greater concentration and diversity of contaminants, due the large number and variability of sourcing points. This presents a major challenge, compounded by the fact that more sophisticated applications (including catalytic processes for bioH<sub>2</sub> production) have low tolerances. Generally, the design point for the waste composition for a thermochemical facility is derived from a number of datasets for representative residual municipal, commercial and trade waste collected nationally as well as locally. The data presented in the *Supplementary Information* document gives a design point specification of waste sourced in Western-England. Waste cannot be thermochemically treated in the form it is when collected. The untreated municipal or commercial waste is first mechanically processed in a materials recycling facility (MRF). This is done to homogenise the material and remove part of the moisture, recyclables (for example, metals and dense plastics) and reject materials (for example, oversize and inerts). The material is then shredded using tearing motion to achieve a rough shred of waste residues, with a homogenous, pre-determined particle size between 1-50 mm, depending on the gasification reactor requirements. The final feedstock is in the form of floc RDF (Refuse Derived Fuel), which is then further dried on-site using waste heat from the process. Typically, a 150,000 tonnes

MSW feed produces an output of ca. 90,000 to 120,000 tonnes of RDF with a moisture content of 10–17 %, 10–20 % ash content and 15–25 MJ/kg calorific value (CV). MRF plants processing commercial waste (mainly package waste) are usually technically more simple than those processing MSW, with RDF recovery efficiencies of above 80% (Wilén *et al.*, 2004).

A good potential reference WtH<sub>2</sub> plant size could treat around 100,000 tonnes per annum of RDF, this being supplied from a reasonably sized town, accounting for residual domestic, commercial and industrial waste arisings. This is also similar in scale to small conventional energy from waste facilities (Defra, 2014). Bus fleets have been identified as the earliest likely adopters of hydrogen for transport. A typical bus will consume around 5 tonnes per annum of hydrogen. A large depot will operate around 100 buses, i.e. 500 tonnes per annum or 20GWh. This equates to around 5% of the WtH<sub>2</sub> plant scale identified. This suggests that transport applications in the medium term are likely to be serviced by slip streams from larger plants designed to service grid or industrial customer applications.

### **2.3 Syngas generation**

The key element for a consistent quantity of bioH<sub>2</sub> is the production of a high quality syngas very rich in hydrogen, and suitable for catalytic processing. Ideally, this syngas is free of poisoning contaminants (sulphur and chlorine), tars and nitrogen, the latter difficult and costly to remove from a gas stream product. In order to get the right syngas, both autothermal and allothermal processes can be used. The chemistry and form of the feedstock, as well as scale, means that unlike coal, RDF cannot be processed using established high intensity technologies, like for example entrained flow gasification (Materazzi *et al.*, 2018). Due to their flexibility and robustness, fluidised beds are instead more suitable for small applications and for treating gross and heterogeneous feedstock (Materazzi and Lettieri, 2017b; Arena and Di

Gregorio, 2016). For Waste-to-Gas applications, autothermal fluidised bed processes need to be carried out with pure oxygen as gasification agent. In order to deliver sufficient pure oxygen without getting to high temperature, oxygen/steam mixtures are typically used in practical applications. This will result in a product gas with medium calorific values, very low nitrogen, medium to high hydrogen, and low hydrocarbon contents (mostly methane in few percent) in the product gas. The H<sub>2</sub>:CO ratio is important for further hydrogen separation, as low values are likely to cause low bioH<sub>2</sub> yield and high CO<sub>2</sub> generation during water gas shift. In case of oxygen-steam gasification, H<sub>2</sub>:CO will be in the order of 1.0 to 1.5 depending on waste : steam ratio or moisture content. Moisture in autothermal reactors is normally limited to below 15%wt. When high quantities of moisture are present in the initial RDF, the oxidant supply rate must be enhanced to generate sufficient heat to sustain the gasification reaction, resulting in lower syngas heating value (Materazzi *et al.*, 2016a). As temperature within the bed has to be limited to below ash softening point, upstream oxygen enrichment can also be used, although issues arise for the potential hazards associated with oxygen-rich mixtures at high temperatures (Leclerc and Larachi, 2015).

Allothermal gasification processes will typically use steam, or in future CO<sub>2</sub>, as gasification agents in an externally heated reactor, fast internally circulated fluidised beds (FICFB) or dual fluidised beds (DFB) (Wilk *et al.*, 2011; Leclerc and Larachi, 2015). In this latter configuration, air is used to burn char and/or secondary fuels in a separate chamber to provide heat to an inert bed material (e.g. sand) which is then transferred to a second oxygen-starved unit running in parallel on steam (or CO<sub>2</sub>). Since the process is split in two separate chambers, the produced syngas is not diluted with products of combustion, and CO<sub>2</sub> and N<sub>2</sub> content within the syngas is significantly low. The focus of industrial work on bioSNG production, for

example, has largely focused on utilising this type of indirect gasification technologies (Rehling *et al.*, 2011). In principle, these offer a significant thermochemical efficiency advantage for bioSNG production, providing a syngas with as much as 15% methane. However, this advantage often reflects higher propensity to tars production, as methane is simply the gaseous end of a spectrum of complex and condensable hydrocarbons produced, including volatile organic carbon (VOC), sulphur-containing organic species and condensable oils, which need to be removed (with some inevitable loss of chemical energy from the syngas) (Materazzi *et al.*, 2014). Promising results for a beneficial product gas for bioH<sub>2</sub> production are obtained with steam as gasification agent, this leads to medium calorific values and high hydrogen content in the syngas (H<sub>2</sub>:CO close to 2.0). CO<sub>2</sub> as gasification agent compared with steam as gasification agent will lead to lower hydrogen and higher carbon monoxide contents and consequently to an essential lower ratio of H<sub>2</sub>:CO (Tancredi *et al.*, 1996).

Another class of allothermal gasification technologies include plasma, often used in combination with other reactors (Fabry *et al.*, 2013). The use of plasma has increasingly been applied with waste treatment for its ability to completely decompose the input material into a tar-free synthetic gas and an inert, environmentally stable, vitreous material known as slag. The principal advantages that plasma offers to thermal conversion processes, besides the already mentioned tar/ash related issues absence, are a smaller installation size for a given waste throughput, and the use of electricity as energy source, characteristics which permit the technology to treat a wide range of heterogeneous and low calorific value materials. This include various hazardous wastes, such as polychlorinated biphenyls (PCBs), medical waste, and low-level radioactive (Gomez *et al.*, 2009; Wang *et al.*, 2009; Byun *et al.*, 2010; Lombardi

*et al.*, 2015; Sanlisoy and Carpinlioglu, 2017). Vitrified ash products show excellent mechanical and anti-leaching properties, and are suitable as a construction material (Wang *et al.*, 2009). Stand alone or two-stage plasma processes are particularly suitable for processing waste feedstock due to the high quantity of ash, organic and inorganic contaminants, and typical fluctuating quality of the feedstock, notwithstanding that the presence of an air separation unit (ASU) and plasma electrode make the process particularly energy intensive. On the other hand, the issues associated with complex organics and organo-sulphur compounds suggest that indirect gasification has significant drawbacks as a technology for producing syngas to be used in bioH<sub>2</sub> production. However, the advantage of not needing an air separation unit makes these processes attractive for less problematic fuels, i.e. pure biomass.

## **2.4 Syngas clean up**

The fuel gas exits the gasification stage at temperature usually higher than 800 °C and comprises mostly H<sub>2</sub>, CO, H<sub>2</sub>O and CO<sub>2</sub> and a number of minor contaminants. After heat recovery, the syngas has to go through a gas cleaning system to remove tars, particulates, vapour phase metals, acid gases (mostly, Cl<sup>-</sup> and S<sup>-</sup> based), and a myriad of trace species released from RDF which could hinder the effective syngas utilization downstream. The cleaning from these problematic species down to values that are acceptable for different downstream catalysts are of crucial importance for successful implementation of waste gasification technology, and in particular bioH<sub>2</sub> applications. These systems are asked to deal with a much wider and heterogeneous range of contaminants compared to other biomass applications, and at the same time respond to more stringent specifications dictated by catalysts for bioH<sub>2</sub> production. The success of new gasification technologies for the treatment of waste feedstocks in the future will be assessed also on this basis.

Copper catalysts for biohydrogen production require a level of the contaminant in the gas phase to be below 0.1 ppm to be considered acceptable for commercial use (Ladebeck and Wagner, 2003). In the case of mercury vapour this is generally required to be below 10 ppb to be acceptable (Dunleavy, 2006). Sulphur compounds are widespread in waste derived syngas and the higher molecular weight compounds (i.e. thiophenes) are reasonably refractory, requiring plasma reforming or high temperature hydrotreatment to be removed. Secondary poisons are the metal hydrides (arsine/phosphine) and acid gas components (HF/HCl). Tertiary poisons are the aromatics and olefins which give rise to polymeric and carbon deposits on the catalyst surface (Seemann *et al.*, 2006). For economic reasons at small scale, the organic sulphur, unsaturated hydrocarbons (e.g. ethylene, acetylene, etc.) and light aromatics arising from lower intensity gasification cannot be removed using physical solvent scrubbing such as Rectisol, and must be dealt with thermal or hydrothermal technologies. When plasma or hydrodesulfurization (HDS) are used, the result is that the remaining contaminants can be removed by a conventional acid and alkali scrubbing. Typical cleaning system for small scale (<100 MW) waste based plants includes tar reforming systems, dry filters (incorporating a ceramic filter unit with chemical sorbents dosing), and alkaline wet scrubbers (Zwart, 2009). The clean syngas is dewatered before being further polished in a series of guard beds for removal of remaining contaminants deleterious to the catalytic process, including dehalogenation, and trace sulphur removal through hydrogenation and desulphurization in ZnO beds (Asadullah, 2014). An extensive review of gas cleaning methods for syngas polishing is provided by several authors (Woolcock and Brown, 2013; Asadullah, 2014; Abdoulmoumine *et al.*, 2015).

## 2.5 Water Gas Shift reactors

Hydrogen produced from gasification is not sufficient to sustain a WtH<sub>2</sub> plant on its own. Additional H<sub>2</sub> is produced by conversion of the CO in syngas through the water-gas shift (WGS) reaction:



This is an exothermic equilibrium reaction with hydrogen production favoured by low temperature, often obtained with two sequential reactors with intercooling stage. The first step is a standard shift catalyst (high temperature shift, or HTS catalysts) which operates at temperatures in excess of 300°C, limiting CO conversion. Ferrochrome (Fe-Cr) oxide based formulations are the most commonly used high-temperature (320-450 °C) HTS catalyst (Ratnasamy and Wagner, 2009). In order to achieve high levels of CO conversion, it is necessary to operate a second step at lower temperatures (190-220 °C), using low temperature shift (LTS) catalysts. The most common LTS catalysts are varieties of copper/zinc oxides supported on alumina substrates (Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>) (Gokhale *et al.*, 2008). Both HTS and LTS catalysts are sensitive to sulphur content, with the latter start deactivating at concentration as low as 1 ppm. Cobalt/molybdenum (CoMo)-based shift catalysts are instead widely used for syngas streams that contain very high levels of sulphur. In particular, these so-called "sour-shift" catalysts are preferred by plants that use low-temperature bulk desulfurization systems, where the shift catalyst must operate upstream of the gas clean-up system in the presence of up to percent levels of sulphur (Ladebeck and Wagner, 2003).

Over 100 years of industrial experience on water gas shift for coal to-liquid or gas to-liquids processes, have taken to a large number of publications, and extensive understanding of syngas requirements and reaction mechanisms (Ladebeck and Wagner, 2003; Ratnasamy and Wagner, 2009; Smith *et al.*, 2010). The aim in the bioH<sub>2</sub> case is, therefore, to push the WGS reaction to a practical limit, while providing a clean and good quality syngas to ensure high catalyst longevity.

## 2.6 CO<sub>2</sub> removal and upgrading

The product from WGS is normally a mixture of H<sub>2</sub> and CO<sub>2</sub>, with some other minor components (N<sub>2</sub>, CH<sub>4</sub>, CO) depending on the upstream processes. There are many commercially deployed techniques for separating CO<sub>2</sub> from process streams with the optimal solution depending on factors, such as the required specification of the product stream, required CO<sub>2</sub> purity, and the temperature and pressure conditions of the inlet and outlet streams. There are two relevant specifications for hydrogen produced by a WtH<sub>2</sub> plant presented in this work, namely: **bioH<sub>2</sub> for use in fuel cells**: 99.95% purity, with additional restrictions on certain contaminants (Shabani and Andrews, 2015); **bioH<sub>2</sub> for use in the gas network**, in industry, or blended into the natural gas network (“grid-quality”): <2% inerts, CO content below 100ppm, some methane can be accommodated (up to 10% vol) (De Santoli *et al.*, 2017; Kouchachvili and Entchev, 2018).

Commercial plants anticipated in the context of this investigation would produce both but, owing to the limited market for transport-grade hydrogen, less than 10% of the output would be at transport quality at this stage. Pressure swing adsorption (PSA) is commonly employed to achieve the 99.95% purity required for use in fuel cells (Asgari *et al.*, 2014). However, several studies have shown that PSA results in significant slip of H<sub>2</sub> into the tail gas, reducing

both product yield and purity of the CO<sub>2</sub> stream (Olajire, 2010). Luberti et al. (Luberti *et al.*, 2014) have shown that hydrogen recovery can reach a maximum of 93 % with a Polybed H<sub>2</sub> PSA system having twelve columns. The tail gas from PSA can be recirculated back into the main process train when upgrading a small slip stream of high purity hydrogen, but this cannot be done for the whole process stream because the CO<sub>2</sub> must ultimately be removed from the system. For this reason and because the CO<sub>2</sub> is not of sufficient quality for sequestration, PSAs might be inappropriate for a small scale WtH<sub>2</sub> plant. Several other separation technologies could be considered, including membrane separation, physical solvents and amine systems (Granite and O'Brien, 2005; Adhikari and Fernando, 2006; Barelli *et al.*, 2008; Shokrollahi *et al.*, 2016). A good potential solution in this application could be a Benfield-type potassium carbonate system as it offers high CO<sub>2</sub> recovery, high CO<sub>2</sub> selectivity and good heat integration, with low electrical loads and pressure drop for product stream (Borhani *et al.*, 2015). As a result, the slip of product into the CO<sub>2</sub> stream is very low, giving good H<sub>2</sub> yields and a captured CO<sub>2</sub> stream at a purity suitable for sequestration.

Following CO<sub>2</sub> removal, there will be residual CO in the bioH<sub>2</sub> stream. At this point, a slipstream can be taken for high-purity hydrogen production in a PSA (the tail gas is reintroduced to the process). The bulk of the gas can instead proceed to a CO polishing methanation stage, with a high-nickel catalyst, where residual CO is converted to methane (Takenaka *et al.*, 2004). The high-activity catalyst ensures that CO levels are reduced to below 100ppm, as requested by grid quality gas. Methane levels in the hydrogen stream can reach 10%; for grid blending and industrial use, this methane content is operationally beneficial (Kouchachvili and Entchev, 2018).

A simplified schematic of the proposed WtH<sub>2</sub> process is shown in Figure 1.

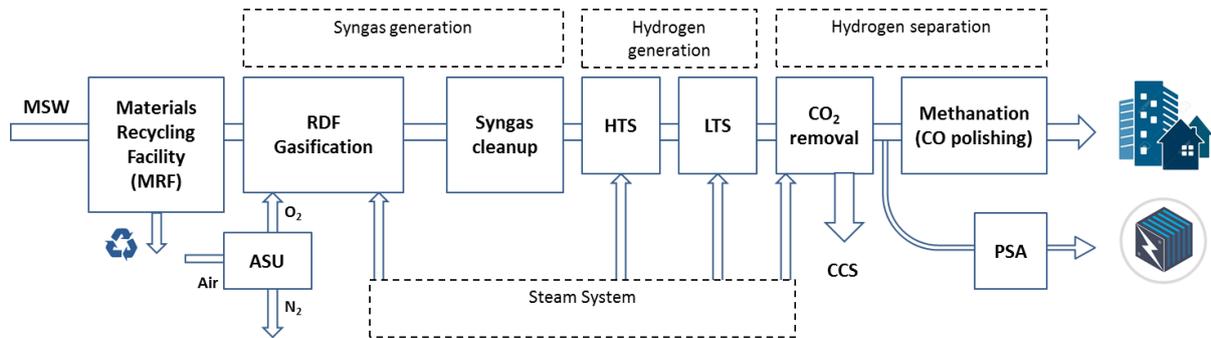


Figure 1 Process flow diagram for a standard commercial WtH<sub>2</sub> plant

### 3. Pilot scale testing

This section reports the results of experimental work and of demonstration of bioH<sub>2</sub> production at pilot scale. The main specific objectives of the work were to characterise potential catalysts for the process, understanding performance and optimal operating conditions for conversion of waste-derived syngas, and to show that residual CO levels in the product can be reduced to near zero. The latter is particularly important to eliminate the possibility of injecting CO into the gas network on account of its known toxic potential. Furthermore, production of biohydrogen at scale was demonstrated, including the processing required to utilise waste feedstock with sensitive catalysts. This information would provide from the foregoing an analytical basis for the definition of a full-scale WtH<sub>2</sub> process.

In pursuit of these objectives, practical investigations and demonstrations were undertaken utilising existing assets from the earlier small-scale bioSNG plant developed in Swindon (UK).

These comprise a 500kW gasification facility, which replicates all of the system elements that would constitute the syngas production train in a commercial-scale plant, as shown in the process flow diagram (Figure 2). The syngas is then used in a second facility on site to prove the production of biohydrogen from real waste derived syngas. A full description of the two parts of the plant is provided in this section.

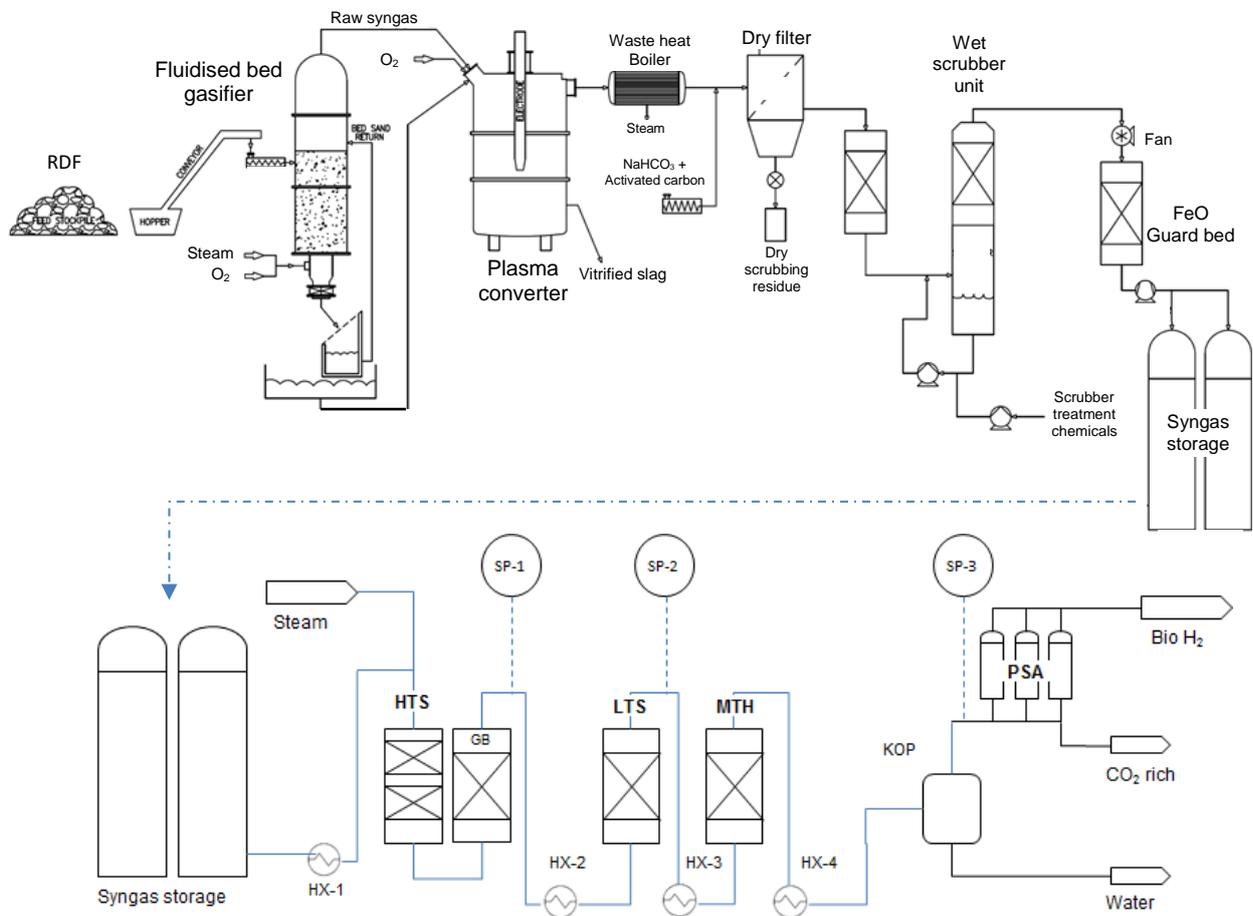


Figure 2: 500 kW pilot gasification plant for clean syngas production (top), 50 kW bioH<sub>2</sub> production from stored syngas (bottom)

### 3.1. Syngas generation plant

The gasification process is a combination of two distinct thermal process steps. The first is a bubbling fluidised bed gasifier operated at 700-800 °C, in which steam and oxygen are used to partially oxidise the RDF. In the second step, the crude syngas produced by the bubbling bed gasifier is refined in a separate plasma converter (Materazzi *et al.*, 2016b). The plasma converter completely degrades complex hydrocarbons and tars reducing them to a clean syngas stream along with simple inorganic contaminants such as hydrogen sulphide and hydrogen chloride, which are readily removed with conventional gas scrubbing techniques. The choice of a two-stage process is not imperative, but it ensures the production of a consistent quantity of syngas from a chemically and physically heterogeneous feedstock, of a quality suitable for chemical transformation as opposed to energy production. With this respect, the reforming action of electric plasma not only ensures stable operation and higher conversion efficiency (due to the conversion of tars and fly char into more H<sub>2</sub> and CO), but also breaks down covalently bound organic sulphur (e.g. thiophenes, thioles, and their derivatives) and other problematic contaminants which would be hardly removed by conventional scrubbers. Thiophene in particular, although rarely measured in small scale plants, has been found to be particularly detrimental in catalytic systems, even at below ppm levels, due to the high sensitivity of synthesis catalysts to sulphur in all its forms (Rabou and Bos, 2012). Furthermore, the large fraction of ash contained in RDF is recovered as vitrified slag from the converter. The vitreous alumino-calcium-silicate matrix of the slag has also been shown to immobilise some hazardous heavy metals and decrease their leachability. The results of the leaching test are reported in other publications and show compliance with limits for inert landfill materials (Materazzi *et al.*, 2015a, Materazzi *et al.*, 2015b). This is a

particularly important aspect in waste treatment facilities because it ensures that only minimum residues (mostly for air pollution control and gas cleaning media) are sent to treatment and disposal (Materazzi *et al.*, 2015a). Downstream of the plasma arc converter, the syngas is cooled to below 200 °C in a heat exchanger prior to treatment to remove any residual particulates and elementary acid gas contaminants (mostly, HCl, COS, and H<sub>2</sub>S). This includes a dry filter (incorporating a ceramic filter unit with sodium bicarbonate and activated carbon dosing), and an oxidative alkaline wet scrubber. This provides bulk removal of nitrogenous compounds, chloride, fluoride, and simple sulphur gases present prior to demisting to reduce entrained water. An iron oxide pellet guard bed is used for any residual sulphur scavenging. Slightly negative pressure (5–10 mbarg) is maintained throughout the process using an induced draft (ID) fan located after the wet scrubber. The outlet of the ID fan defines the system boundary between the original 500 kW<sub>th</sub> gasification pilot facility and the hydrogen production plant. In order to separate the operation of the two plants, the syngas from the gasification process is compressed and stored. The syngas is generated at approximately 0.05 barg pressure and is compressed to 50 barg through a four-stage reciprocating compressor, featuring interstage cooling with condensate removal. The compressed syngas is then supplied to the syngas store, which comprises four identical gas storage vessels. These vessels are capable of holding approximately 1.2 tonnes of compressed syngas, whose composition for the tests reported in this work is reported in Table 1. Details for the operation of the 500 kW<sub>th</sub> gasification pilot facility for syngas generation are reported elsewhere (Materazzi *et al.*, 2018).

Table 1 RDF and Syngas specification used for baseline tests

RDF (as received)	Characterisation of cleaned syngas From storage
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Proximate analysis			Composition:		
Fixed carbon	weight %	6.4	H <sub>2</sub>	vol.%	35.77
Volatile matter	weight %	59.6	CO	vol.%	33.20
Ash	weight %	19.1	CO <sub>2</sub>	vol.%	23.54
Moisture	weight %	14.9	CH <sub>4</sub>	vol.%	1.67
Ultimate analysis			H <sub>2</sub> O	vol.%	0.89
			Other	vol.%	4.90
C	weight %	41.0	<b>TOTAL</b>	vol.%	100.00
H	weight %	5.7	Trace contaminants		
O	weight %	17.5	H <sub>2</sub> S + COS	ppmv	< 50
N	weight %	1.2	Organic sulphur	ppmv	< 30
S	weight %	0.2	Tars (+C6)	µg/m <sup>3</sup>	< 18
Cl	weight %	0.4	Acetylene	ppmv	< 40
Energy Analysis					
GCV ( <i>dry</i> )	MJ/kg	22.1	NCV ( <i>dry</i> )	MJ/kg	8.75

When the second part of the plant (Figure 2, bottom) is in operation for bioH<sub>2</sub> production, this receives syngas from the high pressure store and a heater electrically heats the syngas before releasing the pressure to the required plant operating pressure (in the range 1 to 10 barg). This initial heating is required to prevent the formation of solid, frozen carbon dioxide in the process pipework due to excess cooling during pressure reduction.

### 3.2. Water Gas Shift stages

The syngas is then electrically heated by a further heater (HX-1) to 400°C. A controlled flow of deionised water is added, which is then vaporised to form steam. The steam-laden syngas provides the feed gas to the water gas shift reactor. Because of the small-scale of the plant, heat losses necessitated the use of electric blankets around reactors to ensure components were maintained at sufficient temperature. This will not be necessary on commercial plants where heat losses relative to process thermal loads would be negligible. The HTS comprises a tubular reaction vessel containing a suspended canister containing undiluted catalyst beads, supplied by Johnson Matthey (KATALCO 71-5). The amount of catalyst was selected on the basis of a range of gas hourly space velocity (GHSV) at which the system was close to

thermodynamic equilibrium. At this point residual COS in the gas (if present) would also be hydrolysed to produce H<sub>2</sub>S. The shifted syngas from the HTS passes through a single guard bed tubular reactor (GB) containing a suspended canister of zinc oxide in which any residual sulphur contaminants (principally hydrogen sulphide) within the gas are removed. Some or all of the cleaned, shifted syngas from the Guard Bed passes through a water-cooled heat exchanger (HX-2) so as to cool the gas to a temperature appropriate for that required for downstream second water gas shift (LTS) stage. The LTS reactor is identical in size to the HTS, and filled with Cu-based catalyst (KATALCO 83). During the course of the test programme it became clear that shift reactions alone would not be sufficient to remove CO to the levels required and so the programme was expanded to investigate methanation as a solution to this problem. The cooled shifted syngas is therefore fed to a single methanation reactor of the same size of the previous WGS reactors. A high activity 22% Ni-Ca-Al<sub>2</sub>O<sub>3</sub> (Catal Ltd), mixed with inert alumina beads (50:50 wt.%), was used in MTH to aim at complete CO conversion.

### **3.3. Product Gas Conditioning**

From the final methanation reactor (MTH) the methanation product gas is cooled through a water-cooled heat exchange unit (HX-4) and thence to a knock-out pot (KOP) where any condensed water droplet are separated and removed from the gas stream. This gas mixture is then passed to a pressure PSA unit where the gases are separated from one another to yield a pure H<sub>2</sub> product stream and a carbon dioxide-rich tail gas stream. The plant has been specifically designed to operate over a broad range of conditions, with flows of up to 51 kW (of thermo-chemical energy) of hydrogen product gas, and at reaction pressures of between 1 and 20 barg.

The gas composition is continuously monitored using an IR Xentra 4210 analyser in the gasification facility, a Gaset Fourier Transform Infrared (FTIR) Continuous Emissions Measuring System (CEMS) and Gas Data Click gas analyser in the bioH<sub>2</sub> facility, and in the PSA unit a Siemens Ultramat 23 for CO/CO<sub>2</sub> and a Siemens Calormat for H<sub>2</sub>. Three gas sampling locations SP-1, SP-2, SP-3 were used to measure gas composition using the FTIR, i.e. downstream the HTS, LTS and MTH respectively.

## 4. Results and Discussion

### 4.1. Plant start-up and System tuning

The 50 kW bioH<sub>2</sub> pilot plant was operated for approximately 4 days, with the first 12 hours used for warm up, catalyst reduction and system tuning. The catalytic beds were externally heated at adequate reduction temperature (180-230 °C) and treated in sequence with a continuous flow of bottled hydrogen (20% vol. in N<sub>2</sub>) for several hours until temperature profiles inside the beds were mostly flat. This was the indication that the fresh, oxidised metal catalysts inside the vessels were fully reduced and ready to operate on syngas. Clean syngas from the gas storage vessels was then diverted to the system at increasing flowrate, and between 5 and 7 barg delivery pressure. Controlled flow of water was added to the system immediately prior to the electrical heater. Combined flow of gas through the reactor was sufficient to give a GHSV of between 5000 and 11000 h<sup>-1</sup>.

Symmetrical trends of CO and CO<sub>2</sub> were observed in the first HTS reactor reflecting the occurrence of water gas shift as the dominating reaction from temperatures above 250°C (Figure 3). CO conversion increased from 10% to above 60% as the temperature was increased through the system. Simultaneously, the change in the temperature profile with time-on-

stream in the reactor was stable and in line with expected trends. Temperature profile gradually spread out across the reactor, along with an increase in CO conversion, until reaching equilibrium conditions at  $\sim 340^{\circ}\text{C}$  after  $\sim 4$  hours of operation.

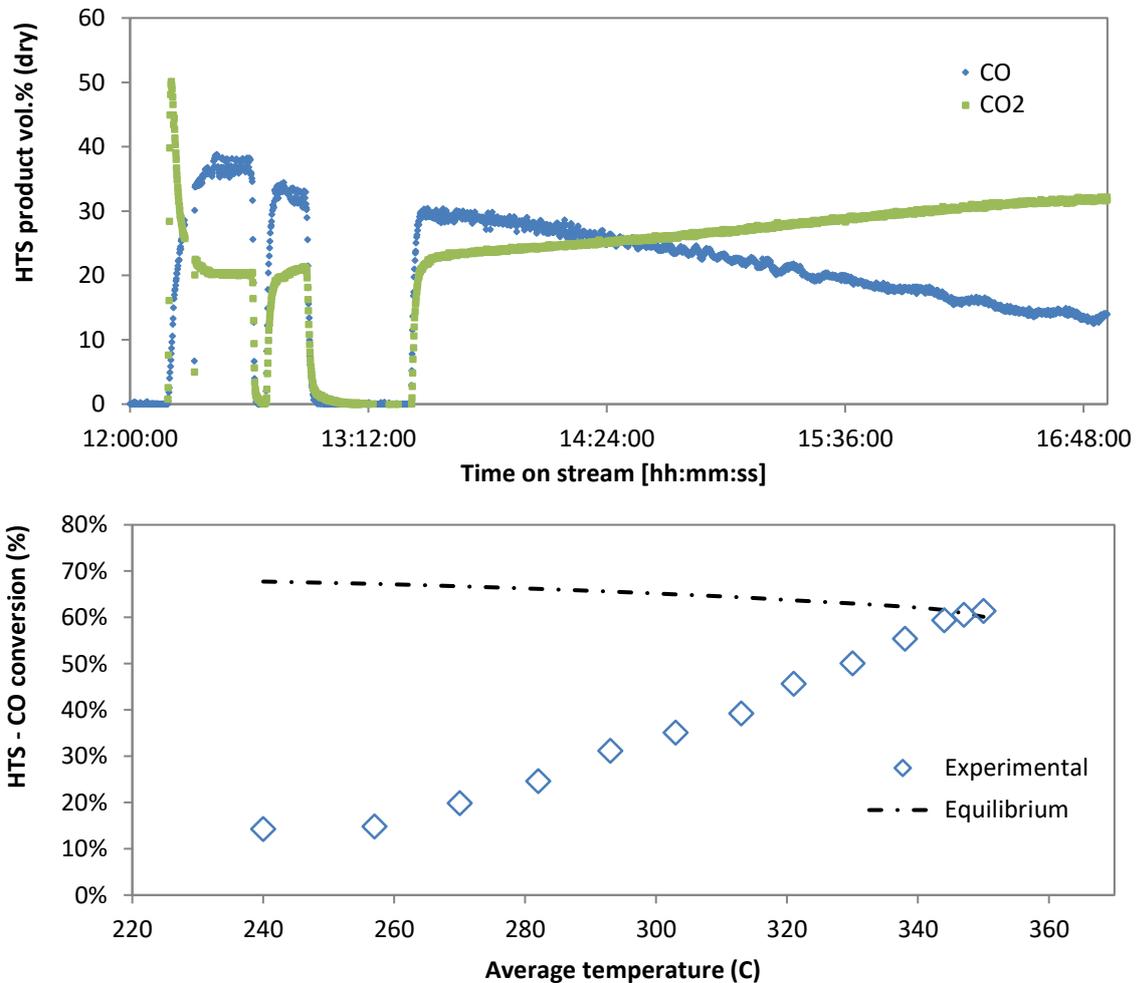


Figure 3: CO-CO<sub>2</sub> measurement (SP-1) and CO conversion recorded during HTS start up (Steam:CO = 1.4, syngas inlet composition as in Table 1, GHSV:7800 h<sup>-1</sup>)

A broad range of conditions were tried but the lowest product gas CO content achieved in the HTS was around 8 vol%, with conversions of CO of 50-60% at 340 °C. Such performance was found even with great excesses of water vapour present. Switching gas sampling location to position SP-2 showed that LTS was also working effectively towards reducing CO. The LTS

reactor is better operated at about 200°C inlet temperature and reduce the CO level from typical inlet levels of 9-10 mol % (dry) to 1-3 mol % (dry). Higher conversion could be potentially achieved for lower inlet CO levels. Different steam:CO ratios were also tested, as shown in Figure 4. As steam is injected before HTS, the curves reflect the enhanced conversion for both HTS and LTS stages. When H<sub>2</sub>O:CO was increased from 1.4 to 2.2 a decrease in residual CO was observed, indicating that a slight excess amount of water helps in pushing the reaction towards the final products.

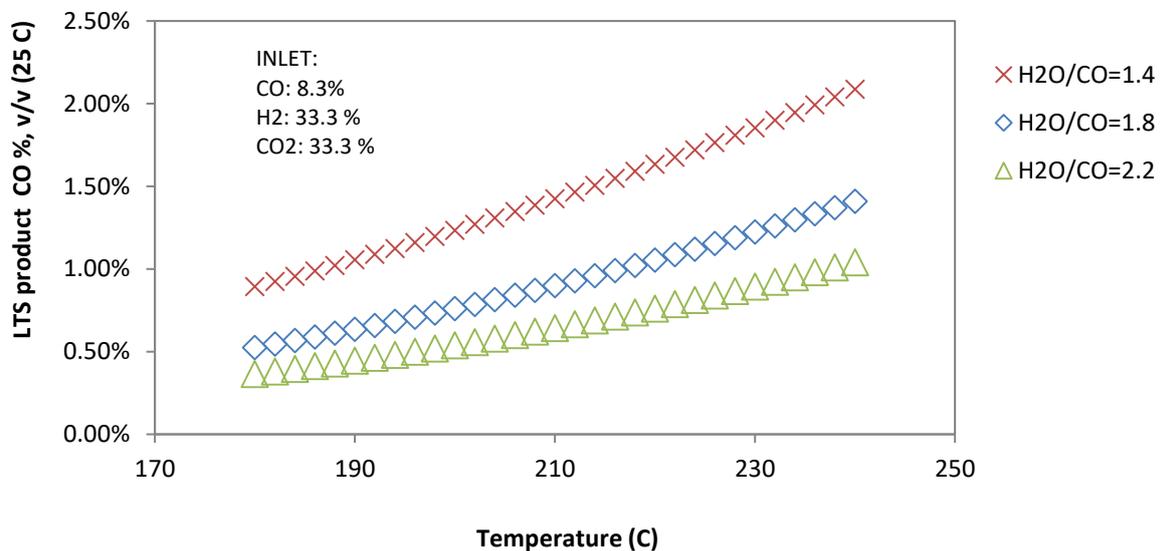


Figure 4 LTS - CO outlet concentration (SP-2) for different H<sub>2</sub>O:CO ratio

Higher H<sub>2</sub>O:CO ratio were not tried as this could have caused pore saturation (Ratnasamy and Wagner, 2009). Excessive steam feeding the WGS reaction has two beneficial effects: it increases equilibrium conversion and disfavours coke formation. It is concluded, therefore, that for the examined catalysts the most appropriate reaction condition is a H<sub>2</sub>O:CO molar ratio of approximately 2.

#### 4.2. Gas compositions at different locations

Figure 5 contains a snapshot of the gas compositions generated throughout the process. Total CO conversion was 92.1% through both HTS and LTS reactors, with the HTS achieving, on occasions, 62%. H<sub>2</sub>:CO molar ratio increased from 1:1 in the syngas from the gas store, to 3.1:1 in the HTS to a final 15.9:1 in LTS product gas. The methanation reactor achieved CO concentrations of below 1%, a value in line with equilibrium predictions and literature data at 230 °C. Close to 100% CO conversion could be achieved with higher Nickel catalyst (40-50% wt.) active at lower temperatures (180-200 °C), or by removing the bulk of CO<sub>2</sub> upstream. Most importantly, no catalyst deactivation could be observed during the 4 days of continuous operation. This confirms that the sensitive catalysts are operating as expected on waste derived syngas in the pilot plant and provides confidence that the proposed production configuration is viable. Future research will focus on further observations on the integrated system, possible catalyst deactivation during long term (> 2000 h) trials, and CO<sub>2</sub> separation by means of chemical processes.

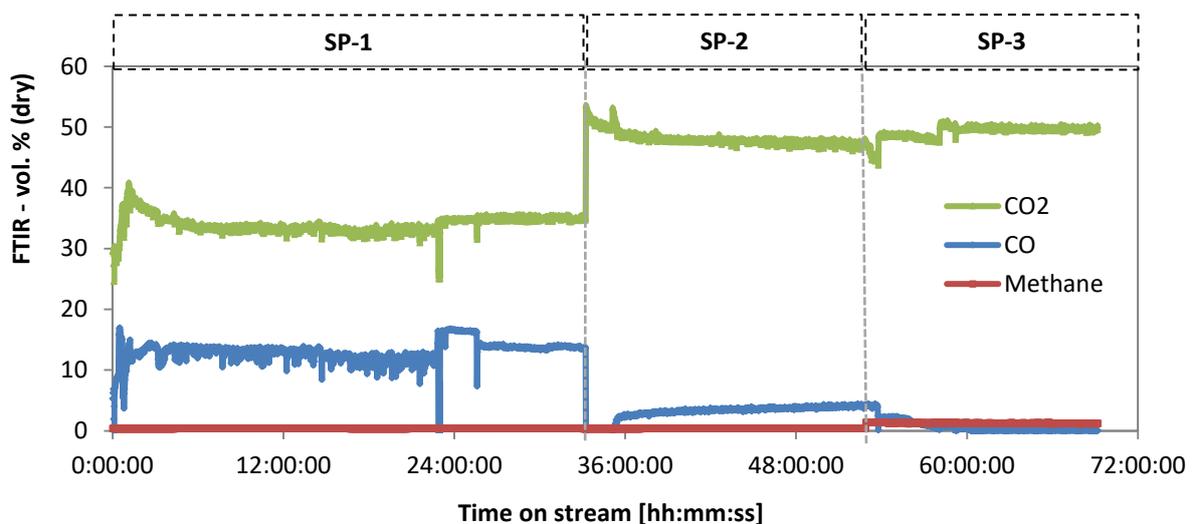


Figure 5 FTIR readings for CO, CO<sub>2</sub> and Methane during entire run at different sampling locations

### 4.3. Full scale Plant considerations

This section summarises the process design for the proposed WtH<sub>2</sub> plant on the basis of pilot plant results, and developed to meet the functional specification described in Section 2. The baseline design is for a commercial-scale WtH<sub>2</sub> plant, producing 360GWh per annum of hydrogen (grid quality) from refuse derived fuel (RDF) or similar biomass-rich feedstock, 23GWh of which would be high-purity hydrogen for use in transport applications. A full mass and energy balance was produced for commercial plant configurations, incorporating process models produced during the experimental work described. The aim of the projection was to establish the environmental benefits of biohydrogen production from waste as represented in Figure 1. Steam and heat generated were assumed to be used internally and not considered, for example, for further electricity production. This allows a more conservative estimation to be provided. Details of the full mass and energy balances of the gasification plant and associated emissions can be found elsewhere (Evangelisti *et al.*, 2015; Tagliaferri *et al.*, 2016; Manson-Whitton, 2017). The energy-basis Sankey diagram and the key parameters for the process model are reported in the *Supporting Information* document.

The cold gas efficiency (CGE) of the process is projected to be slightly lower than 70%, which is in line with those of other biohydrogen plants based on biomass (Ni *et al.*, 2006; Zech *et al.*, 2015). Main differences are due to the additional electrical input for gas cleaning and ash vitrification owed to operation on waste. The quantity of CO<sub>2</sub> captured (~ 18 tonnes per hour) is significantly higher than from other Waste-to-Gas facilities, like bioSNG, meaning that the environmental benefit of bioH<sub>2</sub> production is significantly greater where CCS is available

(Tagliaferri *et al.*, 2016). This is because in the WtH<sub>2</sub> case, close to 100% of the carbon initially present in RDF is recovered as CO<sub>2</sub> product.

To better understand the environmental benefit of bioH<sub>2</sub>, an early assessment of the carbon emissions associated with the process described hereby was attempted. Although a full Life Cycle Assessment was not possible due to the lack of full emissions data of a real commercial plant, a high level estimation of CO<sub>2</sub> emissions associated to production and avoided burdens could be made. The baseline for this analysis considered a commercial plant producing 360GWh/annum of 'grid-quality' biohydrogen from RDF. This is similar to the facility described in previous section, the only difference being that no transport-grade hydrogen is produced (the impact on greenhouse gas performance of this change is minimal). For comparison, the plant was considered with and without carbon capture and storage.

Any analysis of carbon emissions must be clear about the boundary of the system considered, and the counterfactual for CO<sub>2</sub> emissions. In this case, boundaries include emissions associated with production and transport of material inputs and product use. For the CO<sub>2</sub> emissions counterfactual, one approach in the renewables industry is to consider emissions derived from biogenic carbon to be zero and fossil-derived carbon emissions to have the global warming potential (GWP) of CO<sub>2</sub> (Christensen *et al.*, 2009). This approach ignores the particular issues associated with a waste feedstock. In fact, if not treated in thermochemical facilities, waste must be always disposed of, generally either by incineration or landfill. Therefore, these should be the counterfactuals against which waste-to-fuels processes are evaluated. Incinerators convert the vast majority of fossil and biogenic carbon in the feedstock to CO<sub>2</sub>. Taking this as a counterfactual, CO<sub>2</sub> emissions associated with fossil carbon in the feedstock should be discounted because they would have been emitted in any case.

When waste is landfilled the biogenic content decomposes and produces methane, a greenhouse gas 23-25 times as damaging as carbon dioxide. Emissions associated with landfill are therefore far greater than those associated with incineration (Cherubini *et al.*, 2009). A conservative approach is to take incineration as the counterfactual and discount all CO<sub>2</sub> emissions arising from carbon in the feedstock; that is the basis for this analysis. For clarity, the full assessment also considers emissions associated with transport of municipal waste and RDF, production of dry RDF from municipal waste, production of biohydrogen from RDF (electricity, oxygen, chemicals), and final separation and capture of CO<sub>2</sub>, as reported in Table 2. The assumption is made that the product is injected into the national gas grid, with exact pressures depending on plant location, potentially but not necessarily requiring some further compression. Therefore, this is excluded from the calculation. Emissions at the point of use are taken to be zero; emissions arising from small quantities of methane combustion in the mix are ignored because of the incineration counterfactual. The carbon intensity of electricity used in the process is an important factor and is rapidly reducing in the UK. For this analysis, operation in 2020 was assumed and an average taken of the carbon intensities from all four scenarios given in National Grid's 2017 Future Energy Scenarios (FES) (National Grid, 2017). The intensity used was therefore 174kgCO<sub>2</sub>/MWh. Emissions from each process step for the capture and non-capture cases, are given in Table 2, per megawatt hour of bioH<sub>2</sub> on a higher heating value basis. Savings against natural gas are given using the EU grid mix value of 243kgCO<sub>2eq</sub>/MWh (Edwards *et al.*, 2007).

Table 2: Consumption and carbon emissions, per MWh BioH<sub>2</sub> produced

Contribution:	Assumptions:	Emissions (kgCO <sub>2eq</sub> /MWh)		References:
		CCS	No CCS	
<b>Feedstock transport</b>	The waste used in these plants will be collected locally, typically from sites within a 10km radius of RDF processing plant which will in turn be a short distance from the biohydrogen facility.	0.9	0.9	(Evangelisti et al. 2015)
<b>RDF production</b>	Ofgem's UK Solid and Gaseous Biomass Carbon Calculator gives electricity, diesel and sulphuric acid use figures for a range of RDF production configurations (Ofgem n.d.). Figures for an aerobic digestion-type facility have been used	8.1	8.1	(Ofgem n.d.)
<b>Biohydrogen plant</b>	The main emissions associated with the WtH <sub>2</sub> plant itself derive from :			
<b>Electricity</b>	Imported electricity for plasma, compressors, and other ancillaries (0.148MWh/MWh with CCS, 0.122MWh/MWh otherwise)	25.8	21.2	(Tagliaferri et al. 2016; Evangelisti et al. 2015)
<b>ASU</b>	Oxygen production (103kg/MWh)	12	12	(Tagliaferri et al. 2016; Evangelisti et al. 2015)
<b>Chemicals</b>	Adsorbants, catalysts, etc.	3.4	3.4	(Tagliaferri et al. 2016; Evangelisti et al. 2015)
<b>CO<sub>2</sub> capture</b>	The biohydrogen process captures carbon dioxide at sufficient quality for long-term sequestration	372 (captured)	-	(Von Der Assen et al. 2014; Northern Gas Networks 2016)
<b>Total:</b>		<b>(322)</b>	<b>46</b>	
<b>Total saving versus natural gas</b>	Natural gas EU grid mix value: 243kgCO <sub>2eq</sub> /MWh	565	198	(Edwards et al. 2007)

The total figures compare well with those for bioSNG calculated in another study, with a 462kgCO<sub>2eq</sub>/MWh saving with carbon capture (211%) or 207kgCO<sub>2eq</sub>/MWh (85%) without (Tagliaferri *et al.*, 2016). In addition, hydrogen from electrolysis results much more carbon intensive. Assuming a commercial electrolyser efficiency to be 50 kWh/kg H<sub>2</sub>, and the same CO<sub>2</sub> emissions associated to use of electricity, approximately 220 kg of CO<sub>2</sub> equivalent are emitted per MWh of hydrogen produced, as also shown in (Bertuccioli *et al.*, 2014). WtH<sub>2</sub>

plant without access to sequestration has significantly lower emissions (by approximately 75kgCO<sub>2eq</sub>/MWh). SMR-derived hydrogen results in a 59% saving, according to another study (Northern Gas Networks, 2016); using the same emissions factors as in this assessment would give 51% savings (saving 123 kgCO<sub>2eq</sub>/MWh). The analysis clearly shows the advantage of biohydrogen production from waste in this case too. When compared with SMR hydrogen with CCS, a WtH<sub>2</sub> plant without access to sequestration has significantly lower emissions (by 75kgCO<sub>2eq</sub>/MWh). Where a WtH<sub>2</sub> plant can access CO<sub>2</sub> sequestration it achieves substantial negative emissions of 322kgCO<sub>2eq</sub>/MWh, which is 442kgCO<sub>2eq</sub>/MWh lower than SMR with CCS and 540kgCO<sub>2eq</sub>/MWh lower than hydrogen from electrolysis. The comparison between carbon emissions of all H<sub>2</sub> production pathways is illustrated in Figure 6. It is worthwhile noting that with projected decarbonisation targets in both the UK and Europe, this conclusion could be reversed in the future and grid connected water electrolyzers can offer significant carbon benefits per unit of hydrogen.

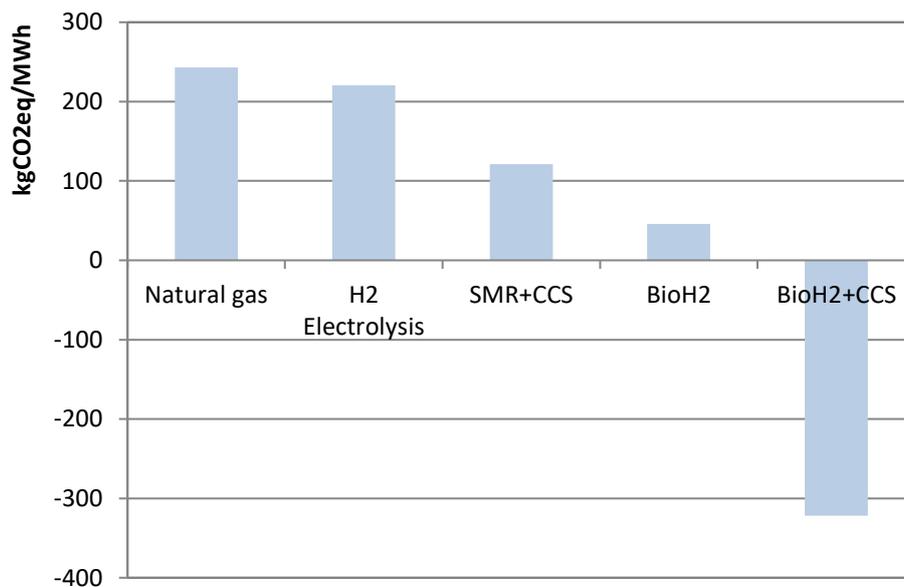


Figure 6 Carbon intensity of different gas production methods

The economics of the three processes (electrolysis, SMR and WtH<sub>2</sub>) are quite different, and an accurate economic analysis was beyond the scope of this work. According to a recent report, as the technology matures, a commercial waste bioH<sub>2</sub> plant should produce a gas with a similar levelised cost to hydrogen produced by SMR with CCS, and significantly lower than the cost of hydrogen produced by electrolysis using off peak electricity (Manson-Whitton, 2017). This is because, as for other thermochemical plants, a WtH<sub>2</sub> plant has relatively high capital costs but operating costs are subsidised by the waste gate fees. On the other hand, capital costs for SMR are lower but the cost of the natural gas feedstock makes operating costs high. Similarly, the significant operating costs for electrolysis are driven by the costs of electricity (Ogden, 2018). The key advantage of biohydrogen is the depth of decarbonisation it offers when combined with CCS. This high GHG saving results in very low costs for each tonne of carbon dioxide saved.

The key disadvantage for WtH<sub>2</sub> is that its potential is limited by the availability of sustainable feedstock. This could be supplemented by imported biomass but the imported volumes are hard to forecast. If CCS infrastructure is developed then wholesale conversion of parts of the gas network may take place, as also described in (Northern Gas Networks, 2016). If this is the case, then biohydrogen should be able to compete with SMR on cost while offering significantly increased CO<sub>2</sub> savings.

## 5. Conclusions

Low carbon hydrogen is seen as a key element of the future energy mix mostly because it generates no greenhouse gas emissions at the point of use. Understanding the technologies

that can generate low carbon hydrogen is essential in planning the future gas network and energy generation via fuel cells. One promising approach is hydrogen production by gasification of waste, referred to as biohydrogen. This work sought to lay much of the groundwork necessary to understand how WtH<sub>2</sub> can be developed, and biohydrogen deployed. Early commercial WtH<sub>2</sub> plants would better be designed to service grid or industrial customer applications. In the medium term, transport applications could be serviced by slip streams from larger plants.

An experimental campaign was undertaken on a modified plant originally designed for bioSNG production. The work has confirmed that the combination of steam-oxygen fluidised bed gasification and plasma refining delivers a high quality raw gas with very low levels of contaminants, while dealing at the same time with the increased amount of ashes by producing a vitrified inert product. The downstream gas processing and polishing techniques have been shown to provide syngas of sufficient quality for catalyst operation. During the time of operation examined, there was no evidence of induced degradation, nor other contamination or deactivation. A two-stage water gas shift process and methanation polishing step are able to produce significant yields of biohydrogen and high conversion efficiencies. However, the resulting CO content is not compliant with gas grid regulations, and requires either more active catalysts or bulk CO<sub>2</sub> separation upstream to increase reactants concentrations. Projections on a full scale plant have allowed an early carbon emission assessment to be made. Carbon savings for biohydrogen in a commercial scale are more than four times greater than alternative technologies. The assessment shows that bioH<sub>2</sub> with CCS has a GHG intensity more than 230% lower than fossil gas. Even without CCS, bioH<sub>2</sub> offers an 82% reduction in emissions. Importantly, it offers the potential for substantially lower emissions than both electrolysis and SMR-derived hydrogen.

In the future, a combination of different hydrogen production technologies associated with CCS could be able to meet the UK's entire gas demand with zero net emissions: the emissions from electrolysis or SMR with CCS would be balanced by the negative bioH<sub>2</sub> emissions and increased share of renewable energy in the electricity mix.

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