

Energy for Business

Innovate and Collaborate with the University of Nottingham







PhusionH2 Ltd

Potential Markets for Hydrogen-on-Demand Generators and their By-products



Executive Summary

PhusionH2 have developed hydrogen (H₂) generators that are based on the chemical reaction between aluminium (AI) or iron (Fe) and water. The proposed system has a potential to offer a low cost solution to H₂ production contributing to the decarbonisation of various applications. The Energy Innovation and Collaboration (EIC) team reviewed the potential markets for the H₂ generators; industrial applications such as ammonia and methanol production, hydrogen-cooled electrical generators in power plants, material handling equipment, back-up power, H₂ refuelling stations, decarbonisation of heat and onboard generators. Amongst those, existing industrial processes relying on H₂ feedstocks such as ammonia and methanol production and hydrogen-cooled electric generators, which could also benefit from low cost on-site generation, could be early markets.

Other potential near-term H_2 markets are material handling equipment and back-up power where hydrogen fuel cell (FC) systems can provide significant operational advantages and potentially economic benefits compared to conventional options. Other FC-dependant H_2 market is H_2 refuelling stations (HRSs). It is projected that the penetration of H_2 vehicles will be in the region of 40-75 % by 2050. This market highly depends on policies restricting greenhouse gas (GHG) emissions and air pollution as well as reductions in the technology cost. Blending H_2 with the conventional fuels such as diesel could help reduce emissions from existing engines as a short-term solution before the H_2 vehicles and HRSs become widely available. Decarbonisation of heat, on the other hand, does not rely on the penetration of FC systems in the market and H_2 is considered as a long-term solution for deep decarbonisation of heat.

The carbon footprint and cost of H₂ generated through Hydrogen-On-Demand (HOD) systems will depend on the source of energy and feedstock used for the reaction. Production of recycled Al only requires about 5 % of the energy needed to manufacture the primary Al from bauxite ores, providing a significant energy reduction and corresponding decrease in the GHG emissions. In addition, recycling of Al eliminates mining requirements, pollutants and wastes associated with primary Al production. Therefore, using recycled Al as a feedstock for the HOD system has a potential to provide sustainable, low cost H₂ with a low carbon footprint.

This reports also provides a brief overview of the potential markets for the by-products generated by PhusionH2 HOD systems, i.e. aluminium hydroxide or iron oxide, with a view that these by-products could also find applications in the market.

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1. Introduction

Hydrogen (H₂) can play a significant role in deep decarbonisation of various sectors. One of the challenges with H₂ economy is the production cost. A wide range of techniques can be used to produce H₂ from different resources. Figure 1 compares H₂ production cost through different pathways. Amongst different techniques, the steam methane reforming (SMR) is the most commonly used method due to its maturity, lower cost and suitability for large-scale production [1]. Currently, approximately 50 % of the global H₂ is met by SMR [2], followed by oil reforming at 30 % and coal gasification at 18 % [3]. However, utilization of fossil fuels to generate H₂ leads to carbon dioxide (CO₂) emissions and is not sustainable since fossil fuels are subject to depletion. Although CO₂ emissions can be captured and stored in depleted natural gas and oil wells or in geological formations, carbon capture and storage is still in the development stage and it increases the system complexity and costs [4, 5].

The cost of H₂ generated through water electrolysis technique, on the other hand, highly depends on the electricity costs. Although there are no direct CO₂ emissions associated with the water electrolysis, the carbon footprint of generated H₂ depends on the emissions resulting from the electricity generation. The water electrolysers coupled with renewable electricity offer a very promising solution to production of low carbon and potential low cost H₂. However, substantial cost reductions in the technology still need to be achieved to make them widely available.

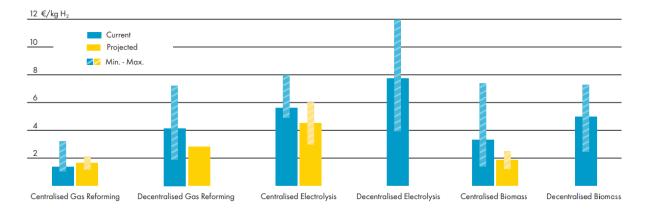


Figure 1. H₂ production cost through different pathways [6].

PhusionH2 Ltd have developed H₂ generators in collaboration with Phillips Company 4T (research and development sister company based in the United States), referred to as hydrogen-on-demand (HOD). They are based on the chemical reaction between water and a metal such as aluminium (Al) or iron (Fe):

$$2AI + 6H_2O \longrightarrow 2AI(OH)_3 + 3H_2$$
 Equation.1
 $3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$ Equation.2

They use electro-activated carbon as a catalyst material to improve the H_2 generation rate. They had initial lab-scale testing in collaboration with Dublin City University. Their design has been patented in the US (Patent number is US 9,102,529 B2) and Japan and patent applications have been made in 16 other countries including the UK. The proposed system has a potential to offer a low cost solution to H_2 production for a wide range of applications contributing to the decarbonisation of various sectors of the economy. The EIC team at the University of Nottingham have reviewed the potential H_2 markets for HOD systems with the focus being on the UK and the EU.

As shown in Equations 1 and 2, the reactions between AI or Fe and water also produce aluminium hydroxide (AI(OH)₃) or iron oxide (Fe₃O₄) respectively as a by-product. Therefore, this report also gives a brief outline of the potential markets for these by-products. As AI(OH)₃ can be used as a feedstock to produce aluminium oxide (AI₂O₃), a short overview of AI₂O₃ markets has also been included.

This report has also provided information about the primary Al production and issues related to this process with a view to highlighting the benefits of using recycled (or secondary) Al to generate H₂ in HOD systems.

2. Why Hydrogen?

H₂ is the most abundant of the elements and offers several benefits as a highly flexible energy carrier. Like electricity, H₂ is an "energy carrier" and can be used in a full range of applications in all sectors of the economy: transportation, power, industry, and buildings [7]. It has the highest energy content per unit mass (141.6 MJ.kg⁻¹) amongst any fuels [8]. For instance, the gravimetric energy content of H₂ is about 3 times more than that of petrol [4].

Utilization of H₂ as a fuel can avoid air pollution and the release of greenhouse gas (GHG) emissions, as the combustion and electrochemical oxidation of H₂ produces water only. This is particularly important for the transport sector which accounted for 32 % of the world's total

energy consumption in 2018 [9]. The internal combustion of H₂ to run a vehicle has an efficiency of about 25 % [10], whilst electrochemical oxidation of H₂ through a fuel cell (FC) system, that converts the chemical energy of H₂ directly into electricity, offers energy fuel conversion efficiencies up to around 60 % [8].

H₂ is not found free in nature, but it can be extracted from a variety of resources including water, biomass and hydrocarbons, making it very attractive when looking for solutions for a sustainable energy future [11]. The 2015 IEA Technology Roadmap for H₂ and Fuel Cells recognizes that H₂ with a low-carbon footprint has the potential to facilitate significant reductions in energy-related CO₂ emissions [7]. Therefore, using renewable and green feedstocks for H₂ production is very attractive from the environmental point of view.

Considering significant growth of intermittent renewables such as solar and wind energies in the World's energy mix, H₂'s relationship to renewables as an energy storage medium cannot be overemphasized. Excess energy from renewables can be used to generate H₂ which can be stored and converted into electricity and/or heat when required maximizing the utilization of renewable resources, as well as providing a solution to balancing energy supply and demand. This can also enable sector coupling by converting excess power supply to H₂ for non-power applications in transport, industry and buildings (heat) sectors [7]. In addition, H₂ can be used for difficult-to-electrify applications or applications that currently use diesel such as heavy duty-transport, non-electrified trains, and maritime transport [7].

It is anticipated that H₂ will also play an important role in decentralized power production in a future energy system that is increasingly inclined to consider distributed generation as an option to exclusively centralized power production [7].

3. Hydrogen Markets

The use of H₂ in industrial processes is increasing with various applications. Currently, the majority of H₂ is produced from fossil fuels mainly from natural gas via SMR and mostly used for ammonia production, oil refining, food production, metals treatment, chemical and metallurgical industries and space programs [12, 13].

The development of H₂ production technologies requires identification of potential markets and the constraints associated with those markets. The major future markets for H₂ depend primarily upon four factors [14]:

- the future cost of H₂,
- the rate of advancement of various technologies that use H₂,

- potential long-term restrictions on GHG emissions, and
- the cost of competing energy systems.

For low carbon H₂ production technologies, potential restrictions on CO₂ emissions to the atmosphere are a key factor in the possible size of future markets. This section gives potential markets for HOD systems including industrial markets, hydrogen-cooled electrical generators, materials handling sector, back-up power, hydrogen refuelling stations, on-board vehicle applications and decarbonisation of heat.

3.1. Industrial Markets

H₂ has long been utilized in industry, either as a feedstock or as a by-product of an industrial process. H₂ is required in several industrial markets including chemical industry such as ammonia and methanol production, fertilizer for agriculture, H₂ welding, metallurgy, glass, food processing, electronic industry, pharmaceuticals and utilities [7, 15]. H₂ is also used in the refining industry for hydrocracking and desulphurization [7]. H₂, as an industrial gas, is already a big global business accounting for more than 90 % of the total H₂ market share.

Chemical industry represents about 63 % of the total industrial H₂ demand [16]. As shown in Figure 2 amongst the chemical industry, ammonia production is by far the largest consumer accounting for around 84 % of the total demand followed by methanol production with a 12 % share.

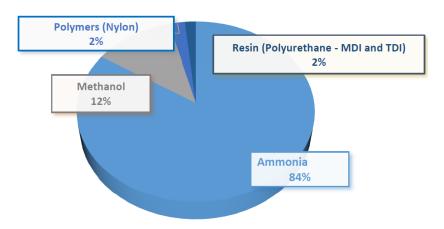


Figure 2. Chemical industry demand by main sub-segments [16].

A typical ammonia plant with a production capacity in the range of 1,000 to 2,000 tonnes per day would need a H₂ feedstock to operate, ranging from 57,500 to 115,000 tonnes per year [16]. As demonstrated in Figure 3 the H₂ demand for current ammonia production is met by the SMR process, resulting in high energy consumption and large quantities of GHG emissions. Ammonia production relies on fossil fuels such as natural gas and accounts for

1.6 % of global CO_2 emissions [17]. Therefore, there is a requirement for low carbon and sustainable H_2 feedstock for the ammonia industry.

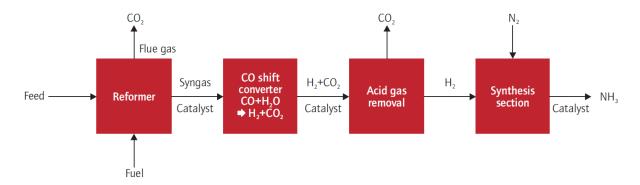


Figure 3. A simplified schematic of ammonia production [18].

Similar to ammonia production, methanol production is also supplied with H₂ through the SMR process. Since it is a mature market, it is forecasted that it will maintain a stagnant growth in the next years [16]. An average methanol production plant with a capacity of approximately 5,000 tonnes per day has an annual H₂ consumption of 266,104 tonnes [16].

Refineries represent the second largest consumer of H₂ within the industry markets at a market share of 30 % (2.1 Mt H₂ per year) [16]. In refineries, H₂ is used for hydrogenation processes to crack the heavier crudes and increase the hydrogen ratio in the molecules and thus produce lighter crudes. The H₂ demand of a refinery site varies greatly depending on the processes involved and products generated. A typical refinery plant operates with H₂ consumption in a range of 7,200-108,800 tonnes per year, while more complex and large refineries can utilize up to 288,000 tonnes H₂ per year [16].

 H_2 is also used in **metal processing**, with a market share of 6 % within the industry markets (410,000 tonnes per year) [16]. The typical H_2 usage in this type of plant ranges between 36-720 tonnes per year [16]. It must be noted that for a metal processing plant that uses H_2 for iron reduction would not be a sensible application for the HOD systems that react Fe with water to generate H_2 .

Other industrial applications for H₂ are semiconductors, aerospace, glass and heat treatment which in total account for 1 % of the industry market share [16].

3.2. Hydrogen-Cooled Electrical Generators

The heat generated during the operation of power generators should be continuously removed in order to avoid damage that can be caused by over-heating of various parts of the generator and to winding insulation. Often, air is circulated through an open or closed circuit

cooling system to control the temperature of the generators. Alternatively, H₂ gas is used as a coolant in a closed circuit system especially for the large scale applications. This is because H₂ has a high specific heat and the highest thermal conductivity of all gases, at about 7 times more than that of air at room temperature [19]. H₂ also has a very low viscosity, which is a favourable property for reducing drag losses in the rotor [19]. Many power generators over 150 MW in capacity utilize H₂ coolers to transfer heat from the power generators to the heat exchangers [20] as hydrogen-cooled power generators are more efficient and smaller than air-cooled options.

The amount of H₂ gas used is usually a function of the power generator capacity and the condition of the generators H₂ seals, with the higher the capacity, the higher H₂ pressure required for sufficient heat transfer [20]. Higher pressure results with higher leakage rate, requiring a higher H₂ flow to maintain the pressure required for optimal heat transfer [20]. Generators with a capacity in the range of 150-250 MW coupled to gas turbines or the steam turbines of combined cycle power plants typically consume 5.7-17.0 Nm³ H₂ per day [20]. H₂ demand can be as high as 25 Nm³ per day for power generators of 400 to 1,200 MW when coupled to steam turbines at thermal plants such as coal fired or thermonuclear plants [20]. Table 1 gives examples of gas-fired combined-cycle power stations from different regions in the UK that utilize hydrogen-cooled generators.

Table 1. Examples of gas-fired combined-cycle power stations in the UK with hydrogen-cooled power generators.

Power station	Total plant capacity (MW)	Location
Carrington Gas-fired power station	880	Manchester
Spalding Power Station	860	Spalding, Lincolnshire
Grain power station	1,275	Isle of Grain, Kent
South Humber Bank Power Station	1,365	Stallingborough
Staythorpe power plant	1,650	Staythorpe
Pembroke power station	2000	Pembroke, Wales

Worldwide, the hydrogen-cooled generators market is being driven by the increasing demand for effective power generators [21]. The growth of the market is also being supported by new upcoming power projects and the restructuring of existing plants [21]. Moreover, technological advancements, which have enhanced the performance of power generators, have been a key factor driving the growth of the hydrogen-cooled generators market [21]. However, the safety is the main challenge for hydrogen-cooled generators.

 H_2 is typically supplied to the power plants by trucks in high pressure cylinders or bulk vessels known as tube trailers. H_2 is then transferred at the plant either by:

- swapping the empty cylinders for full ones,
- swapping an empty tube trailer for a full one,
- transferring from a high pressure tube trailer truck to nearly empty cylinders at the power plant, or to nearly empty high pressure vessels or tube trailers installed at the site [20].

This results in safety concerns and high operating costs as well as dependency on the H_2 delivery in other terms security of supply. Alternatively, H_2 can be generated on-site which can eliminate or minimize the H_2 deliveries by truck, therefore reducing the risk of accidents. With on-site H_2 generation, all piping is permanent and there are no manual connection and disconnection activities associated with the refilling of large volumes of H_2 or transfer operations of truck deliveries [20]. Furthermore, generating H_2 on-site should be less costly per unit volume over time.

Another benefit of on-site generation is that it avoids the need for a high pressure H₂ storage. The H₂ generator can be sized to meet the daily supply. During maintenance activity inert gases are purged out with H₂ gas after the completion of works [20]. This often takes few hours and can take up to 395 m³ H₂ depending on the model and capacity of the generator [20]. In most plants, a large number of cylinders and/or bulk high pressure storage are used for this activity [20]. However, when using an on-site generator the H₂ purge can be supplied by bulk low pressure tanks that are filled with the excess H₂ generated on-site.

3.3. Material Handling Equipment

One of the near-term markets for H₂ powered fuel cells (FCs) is material handling equipment. There is an increasing sale of FC forklifts for industrial uses. In the US alone about 11,600 forklifts were sold as of October 2016 [7]. There are several demonstration projects ongoing around the world including HyLIFT-EUROPE which is the largest European trial of H₂ FC material handling vehicles. This demonstrated more than 200 FC material handling vehicles and their associated refuelling infrastructure across the Europe [22].

Typically, material handling equipment is powered by petrol, propane, or diesel-fuelled engines for outdoor operations or by using lead-acid batteries for indoor applications where emissions must be controlled [23]. Although lead-acid batteries are an established technology with proven reliability, there are several problems associated with using battery systems including:

- limited driving range
- substantial time to recharge and cool before reuse
- · voltage drops as power discharges
- downtime during battery change-outs
- labour cost of recharging and change-outs [23].

Figure 4 demonstrates a comparison of battery and FC powered trucks with regards to the downtime and operational voltage. FC forklifts eliminate time-consuming recharging and swap-outs associated with the batteries, as they can be refuelled once or twice per day in less than three minutes [24, 25]. In addition, FC forklifts can run up to three times longer than the battery driven options per fill-up. Unlike batteries, they produce a constant voltage, so the forklifts can maintain constant power throughout the workday enabling drivers to move more goods in a given period of time, i.e. more lifts, faster lifts and faster traverses [25]. Therefore, using the FC forklifts instead of battery powered trucks can improve productivity and provide operational and financial benefits. The positive economic impact of the deployment would be significant for large fleets with multi-shift operations [26]. In addition, FC trucks eliminate the need for dedicated battery charging and storage/changing facilities enabling more warehouse space. Another benefit of FC powered trucks is that they can offer longer lifetimes in comparison to lead-acid battery driven options [23].

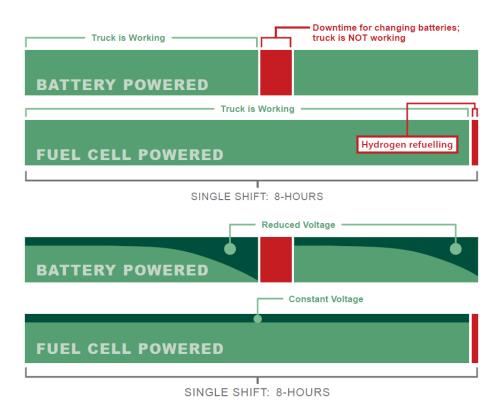


Figure 4. Comparison of battery and FC powered forklifts during a single shift [25].

The H₂ consumption rate of a forklift depends on the type of the truck, e.g. Class I, II and III, the efficiency of the FC propulsion system and workload. Typically, 1.2-1.8 kg H₂ is required to run a FC forklift per shift assuming every shift is 8 h [27, 28]. So the H₂ demand per forklift would be in the range of 2.4-5.4 kg depending on the number of shifts per day e.g. two or three shifts per day. On-site H₂ generators can find a market in material handling applications as a viable H₂ supply eliminating costs and safety concerns associated with delivery or refilling of H₂ cylinders as well as providing security of supply.

3.4. Back-up Power Applications

Another example of an early market for FC technology is in backup power applications which are been increasingly used worldwide in commercial applications. In critical backup power uses, such as data centres and telecommunications stations, even brief power outages can be extremely costly [29]. FC systems have been demonstrated as more viable business cases compared to conventional technologies such as batteries and generators operating on diesel, propane, or gasoline [30]. The drawbacks of the conventional methods are inconsistent power, limited runtime, physical plant issues and high maintenance [29]. FC systems offer the benefits of [31]:

- longer continuous runtime and greater durability in harsh outdoor environments
- fewer moving parts, hence less maintenance requirements
- remote monitoring, reducing the actual maintenance time
- quieter operation with no emissions compared to generators.

The backup power market worldwide is far in excess of 100,000 units annually [32]. Large and increasing numbers of backup power systems are sold for support of computer systems, telecom systems, and other applications. These units represent both new and replacement systems. One of the positive aspects of existing technology used in backup power systems, lead acid batteries, is that the expected life is generally three to seven years [32]. This means the replacement market is a steady and growing segment of the market. In addition, long-term growth rates for telecommunications and computer technology is expected to exceed average economic growth projections [32]. Therefore, the backup power market offers more than enough unit volume to make it economically viable and financially attractive for fuel cell developers [32]. There are a number of FC companies in the market (e.g. Hydrogenics, Proton-Motor, Plug Power, Gencell, Ballard Power, BOC and Pure Energy Centre), selling commercial FC systems for backup power applications at power levels between 1 kW and 100 kW.

H₂ is typically delivered and stored at the point of use as a compressed gas bottles. H₂ delivery cost and availability have been identified as the significant factors affecting the operational costs of FC backup units [33]. Therefore, a low cost on-site H₂ generator could be beneficial for backup power applications, where H₂ delivery is costly and challenging.

3.5. Hydrogen Refuelling Stations

The transport sector accounts for around a third of all final energy consumption and for more than a fifth of GHG emissions in the European Economic Area (EEA) member countries [34]. In 2016, the transport sector contributed 27 % of total EU-28 GHG emissions (The figure decreases to 20 % if international aviation and maritime emissions are excluded) [35]. Transport emissions increased by almost 3 % compared to 2015 level [35], with road transport increasing by 22 % [35]. Emissions need to fall by 20 % by 2030 and around two thirds by 2050, compared to 1990 levels, in order to meet the long-term 60 % GHG emissions reduction target as set out in the 2011 Transport White Paper [35].

Transport is one of the sectors highlighted by the Committee on Climate Change that has made a little progress in decarbonisation. In UK, transportation accounted for the largest proportion of final energy consumption in 2017 at 40 % [36]. In 2017, CO₂ emissions from the UK transport sector, at 124.4 Mt, accounted for 34 % of all CO₂ emissions [37]. Road transport is the most significant source of emissions in this sector, in particular passenger cars, with about 80 % of passenger kilometres being by car, van or taxi [38].

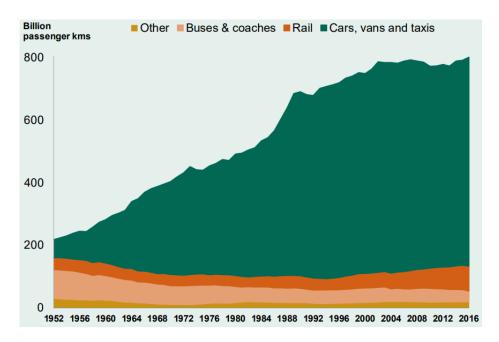


Figure 5. UK passenger kilometres by mode [38].

In addition, air pollution resulting from tailpipe emissions has become a serious problem especially in highly populated areas, taking a growing toll on human health and the environment. The health impacts include various respiratory health problems, lung cancer, eye irritation, allergies, myocardial ischaemia and angina [39, 40]. It is estimated that particulate matter pollution had a mortality impact equivalent to nearly 29,000 deaths across the UK in 2010 [40]. NO₂ pollution has also been a serious issue for big cities, particularly in London, with NO₂ levels similar to cities such as Shanghai and Beijing. An analysis by the Policy Exchange identified that in 2010, 12.5 % of London's area exceeded the legal and healthy limits for NO₂.

Using H₂ as a fuel provides the potential to decarbonize the transport sector and significantly reduce the local environmental impact of vehicles, improving the local air quality thus addressing both environmental and health issues. H₂ fuel can be used via an internal combustion engine or a FC system, with latter being more efficient and resulting in only water as a by-product. FC electric vehicles (FCEVs) use electric motors for propulsion (like a battery electric vehicle (BEV) but generate the electricity using H₂. The main advantage of H₂ over electricity is its greater energy density, which means that FCEVs can travel farther on a single tank of H₂ than a BEV can on a single charge [40]. FC technology could potentially be applied to heavy duty vehicles (HGVs and larger buses) where it will be difficult to apply battery technology due to the weight of the batteries required [40].

A significant number of FCEVs has been deployed in a range of demonstration projects throughout the world. They proved to be very reliable with availability of 98 % achieved [41]. A number of market outlooks have been proposed for the penetration of FCEVs in the EU mobility sector based on different scenarios, using different hypothesis on fuel and technology price evolution and policy support [16]. According to the report published by the Hyways project on the European Hydrogen Roadmap, the penetration of H₂ vehicles would be in the region of 40-75 % for 2050 [42]. It was anticipated that the total oil consumption of road transport could be decreased by around 40 % by the year 2050 as compared to today if 80 % of the conventional vehicles were replaced by H₂ vehicles, this corresponds to a 50 % reduction in CO₂ emissions from road transport by 2050. Details of the results from the Hyways projects can be found in the link below:

https://www.ecn.nl/publications/PdfFetch.aspx?nr=ECN-B--08-006

However, in order to truly recognize the environmental benefits of H_2 as a fuel for vehicles, H_2 needs be supplied from a low carbon source with minimum indirect fuel emissions. Currently, majority of H_2 is produced through the SMR process and delivered to the

refuelling station site in a liquefied form, by tanker truck, or as a compressed gas in cylinders, both of which lead to carbon emissions. Alternatively, H₂ can be generated on-site through a low carbon production method. Decentralized production pathways can reduce emissions, distribution needs and costs. Although on-site generation is more capitally intensive, it may deliver lower cost H₂ [43].

The worldwide count of early market stations open to the public and/or fleets as of mid-2017 exceeds 200 [7], mostly concentrated in North America, Germany and Japan [43]. Information about the worldwide hydrogen refuelling stations (HRSs) can be found in the link below:

https://www.netinform.de/H2/H2Stations/Default.aspx

A wide network of HRSs has yet to be established to meet the demand for increasing numbers of H_2 vehicles. The HRSs with 700 bar dispense pressure are built predominantly for the passengers cars, while 350 bar refuelling technology is used for buses and forklifts [41]. The size of the refuelling station is determined by H_2 demand and coverage area. For example, a station serving 70-100 cars per day would need to supply approximately 0.4 tonnes of H_2 each day [44]. Figure 6 gives predictions for the HRS capacity from 2020 to 2050 based on three main station types.

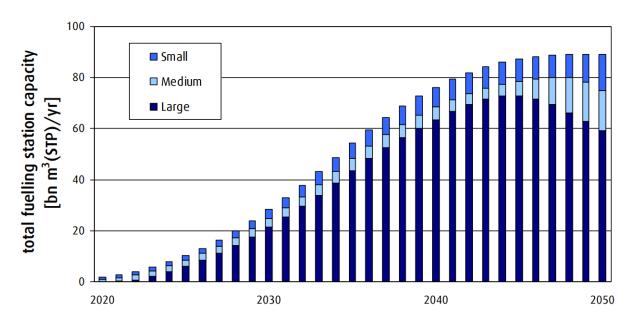


Figure 6. Predicted HRS capacity in the EU region from 2020 to 2050. A small station has a maximum capacity of 0.4 tonnes H₂/day, a medium station with 1 tonnes H₂/day and finally a large HRS, being able to deliver 2.5 tonnes H₂/day [45].

3.6. Decarbonisation of Heat

Heating from all sources accounts for 20 % of UK GHG emissions. Natural gas (which is mainly methane) provides 70 % of this energy, and burning of natural gas for heating contributes 14 % of all GHG emissions in the UK [46]. In its 2017 Clean Growth Strategy, the UK Government presented electricity and low carbon gases, i.e. H₂ and biomethane as two possible ways to provide a future low emissions heating system [46]. The UK Government Hydrogen Innovation Programme aims to resolve the main technical and safety challenges for H₂ gas networks and appliances. There are several projects run by network operators in partnership with industry, look at converting the grid from natural gas to H₂: Leeds H21 City Gate (2016), Liverpool-Manchester Hydrogen Cluster (2017), 100 % Hydrogen (2017–2018) and HyDeploy (2017–2020) [46].

Up to 10-20 % H₂ could be blended into the current gas network, achieving immediate but small GHG savings without changing the infrastructure [46]. The current high pressure tiers of the gas network cannot accommodate H₂, as it could cause the steel pipes to become brittle and prone to leakage. New polyethylene pipes in the lower pressure tiers should make this part of the network more suitable for H₂, and H₂ could be injected into this part of the grid [46]. Under the Iron Mains Replacement Program (IMRP), polyethylene pipes are replacing ageing iron pipework in lower pressure tiers to reduce leakage. The IMRP is due to finish in 2032. Major carbon savings could be achieved rapidly, via a city-by-city programme of converting appliances from natural gas to pure H₂, starting in the late 2020s [46].

3.7. On-board Hydrogen Generators

The addition of H₂ to conventional hydrocarbon fuels especially diesel can improve the performance and reduce the emissions of internal combustion engines (ICEs). Since the combustion of H₂ does not release any carbon emissions, the engine produces less carbon emissions compared to a diesel engine which runs on only diesel. Injecting small amounts of H₂ to a diesel engine could decrease heterogeneity of a diesel fuel spray due to the high diffusivity of H₂ [47]. Mixing of H₂ with diesel in the combustion chamber could also accelerate the rate at which the diesel burns improving the fuel economy [48]. Compared to diesel, H₂ has a wider flammability range, a higher flame speed and a faster burning velocity which enhance the combustion rate of the formed mixture [49]. The properties of H₂ in comparison to diesel is given in Table 2.

Properties Diesel Hydrogen Chemical composition $C_nH_{1.8n}(C_8-C_{20})$ H_2 Auto-ignition temperature (°C) 280 585 Flammability limits 0.7-54-75 (volume % in air) Calorific value (MJ/kg) 42.5 119.9 Flame velocity (m/s) 0.3 2.7 Density (kg/m³) 840 0.082

Table 2. Properties of hydrogen and diesel fuels [48].

Based on the trials in the automotive sector, injecting H₂ into the air-fuel mixture of a diesel engine might improve fuel consumption by 20 to 30 %, reduce particulate matter by 85 % and cut nitrogen oxides by 50 to 90 % [50]. This approach can also find applications in the shipping industry where diesel engines are used almost exclusively. A recent project in Orkney, referred to as Hydrogen Diesel Injection in a Marine Environment (HyDIME), aims to design, integrate and trial an innovative hydrogen/diesel dual fuel conversion system for a 50 kW diesel auxiliary power unit on a car ferry operating between Shapinsay and Kirkwall in Orkney [51].

4. Potential Markets for By-Products

This section gives a brief overview of the potential markets for aluminium hydroxide and iron oxide that are produced as by-products during the reaction between Al/Fe and water. Although aluminium oxide (alumina) is not generated during the reaction in HOD systems, the by-product aluminium hydroxide can be used as a feedstock for alumina production. Therefore, a brief information about alumina markets have also been included.

4.1. Markets for Aluminium Hydroxide

Aluminium hydroxide or aluminium trihydroxide (Al(OH)₃) finds applications as a non-halogen flame retardants. Flame retardants are materials or chemicals that are used to deter or extinguish flame propagation in plastics, resins, textiles, elastomers, coatings, adhesives, and sealants [52]. When exposed to heat, Al(OH)₃ decomposes (at 180-200 °C) to form water molecules in an endothermic reaction, absorbing heat and giving off water vapour in the process [53, 54]:

$$2AI(OH)_3 \rightarrow AI_2O_3 + 3H_2O$$

Equation 3

This dilutes the radicals in the flame, while the residue of aluminium oxide (Al₂O₃) builds up to form a protective layer [54].

As shown in Figure 7, Al(OH)₃ is the largest flame retardant by volume with 38 % of the total market [52]. The global flame retardants market is driven by more stringent international fire protection requirements in the construction sector as well as in rail transport, automotive and the electrical industry, coupled with plastics consumption [55]. Al(OH)₃ is also used as a smoke suppressant for a wide range of polymers, such as polyesters, acrylics, rubber, and polyvinyl chloride (PVC) [53].

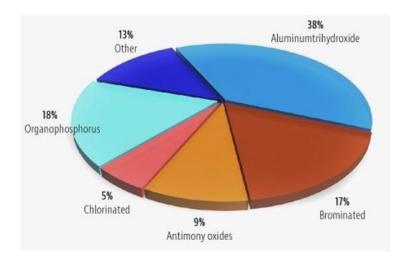


Figure 7. Global flame retardants market by chemistry, 2016 [56].

Figure 8 shows the global flame retardants consumption by region in 2016, with Western Europe accounting for 23 % of the total consumption. The demand for flame retardants in Europe, the Middle East, and Africa is driven mainly by regulations in many industries, such as the building and construction (including housing, public, and commercial buildings) and transportation industries (automobiles and buses) [52]. According to the 2017 market study by IHS Consulting, the consumption of flame retardants has grown substantially in the past four years, notably in electronics, and will continue to grow at a global annualized rate of 3.1 % between 2016 and 2021 [56].

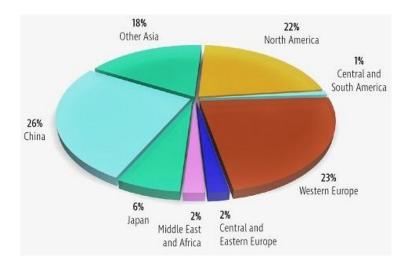


Figure 8. Global flame retardants consumption by region, 2016 [56].

Another main use of Al(OH)₃ is a feedstock to manufacture other aluminium compounds, e.g. speciality calcined alumina, aluminium sulphate, polyaluminium chloride, aluminium chloride, zeolites, sodium aluminate, activated alumina, and aluminium nitrate [57]. It is also used as a compound for several biomedical applications including gastric antacid, antiperspirant, in dentifrices, emulsifier and adjuvant in vaccines [58].

4.2. Markets for Iron Oxides

Iron oxides are mainly used as inorganic pigments for a wide range of applications including [59]:

- coatings (industrial finishes and trade sales coatings: lacquers, paints and varnishes)
- construction materials (cement, mortar, preformed concrete and roofing granules)
- colorants for ceramics, glass, paper, plastics, rubber and textiles
- others (including cosmetics, magnetic ink and toner, and polishing agents).

Iron oxide pigments are non-toxic, relatively inert, weather resistant and mainly opaque [60]. The demand for iron oxide pigments is driven primarily by the construction and automotive industries [60], with the growing construction industry being expected to be one of the most significant drivers for the global market [61]. Iron oxides used as pigments should have a uniform colour, good opacity and be of such hardness that they can be ground to an ultrafine grainsize [60]. The deposits of natural pigments with these properties are unusual, therefore the synthetic pigments are preferred by most manufacturers [62].

Fe₃O₄, also called magnetite, is used as a black pigment referred to as C.I. Pigment Black 11 or Mars Black. It is relatively low-cost and non-toxic compared to other black pigments

[59]. Magnetite is also used as a source of Fe in ceramic applications, particularly in glazing where price and its black raw colour are important and for corrosion resistance purposes, e.g. anti-corrosion paints (used in many bridges, and the Eiffel tower) [63].

In the literature, iron oxides have been extensively used as catalysts in various heterogeneous catalytic processes such as Haber-Bosch to produce ammonia, the Fischer-Tropsch hydrocarbon synthesis, steam reforming, water-gas shift ethylbenzene dehydrogenation to produce styrene monomers, water splitting for hydrogen production, aerobic oxidation of organic compounds to produce new products for the fine chemicals industry and in advanced oxidation processes (AOPs) to oxidize pollutants in water and soils [64].

Iron oxides also find applications in biological and biomedical fields, magnetic separation for industrial water treatment, and in the development of materials for electromagnetic interference shielding due to their magnetic, catalytic, and conducting properties [62]. They are used as a raw material in the ferrite industry. The ferrites are produced by the reaction of iron oxides with any of a number of other metals, including magnesium, aluminium, barium, manganese, copper, nickel, cobalt, or even iron itself. The fields of applications include electronic devices, magnets, and sensors. The concentration of undesirable side and trace elements in the iron oxide material has to be controlled in order to ensure compliance with the high chemical and physical requirements for technical applications of the ferrites [65].

An example of biomedical applications for engineered iron oxides nanoparticles is the magnetic resonance imaging (MRI) where they are used as contrast agents to shorten proton relaxation times [63]. The super paramagnetic contrast agents are composed of a water insoluble crystalline magnetic core, usually magnetite (Fe₃O₄), with a mean diameter in the range of 4-10 nm [63]. Other potential novel applications for iron oxide nanoparticles are [66]:

- drug carriers for target specific drug delivery
- gene carriers for gene therapy
- therapeutic agents for hyperthermia based cancer treatments
- magnetic sensing probes for in-vitro diagnostics (IVD)
- nanoadjuvant for vaccine and antibody production.

According to a market report published by Future Market Insights, the global iron oxide market is expected to increase at a compound annual growth rate (CAGR) of 4.3 % during

the forecast period of 2014 – 2020, reaching an estimated market size valued at around US\$ 1.8 billion by 2020 [67].

4.3. Markets for Alumina

Aluminium oxide (Al₂O₃), referred to as alumina, is the most widely used oxide ceramic material. The worldwide annual production of alumina is about 45 million tonnes with 90 % of this being used to manufacture aluminium metal which is detailed in the following section [68]. Other industrial applications (chemical grade alumina) include filler for plastics, substitute for industrial diamond spark plugs, tap washers, abrasion resistant tiles, and cutting tools [68, 69]. Alumina also finds application in refineries, where the aluminium oxide compound is used to convert dangerous hydrogen sulphide waste gases into elemental sulphur [69].

High purity alumina is a high-end product of the chemical alumina market, serving as a base material for the manufacture of sapphire substrates that are used in various applications such as scratch-resistant artificial sapphire glass, light-emitting diodes (LED), and semiconductor wafers [70]. Demand for high purity alumina is principally driven by increasing implementation of LED products, lithium ion battery separators, sapphire glass for smartphones, and smart watches. It is also used as a phosphor material in plasma displays and as a major component in protective coatings. The price and performance of high purity alumina varies depending upon product density, particle size distribution, and degree of purity [70]. According to a market report published by Persistence Market Research, the global market for high purity alumina is expected to increase significantly at a CAGR of 19.7 % by volume, for the forecast period of 2015–2021 [70].

5. Al Production

HOD systems react Al with water to produce H_2 , therefore the final cost and carbon footprint of H_2 generated depends on the Al cost and environmental impacts of the method used to supply Al. In this section information about the primary Al production is covered with a view of highlighting the importance of using recycled Al to produce H_2 .

5.1. Primary Al Production

Al is the most abundant metal in the Earth's crust. Due to its lightness, resistance to corrosion and ability to be readily recycled, Al is extensively utilised in many applications [71]. Figure 9 shows the Al life cycle. As Al is a reactive metal and is not found in its elemental form in nature, Al is produced from minerals containing Al almost exclusively as

the oxide. Bauxite ores, as Al-rich rocks, are the main source of Al worldwide [71]. They contain hydrous aluminium oxides, aluminium hydroxides, clay minerals, quartz, hematite, magnetite, siderite, goethite, gibbsite (Al(OH)₃), boehmite (AlO(OH)), and diaspore AlO(OH) [71]. They are usually found in topsoil located in tropical and subtropical regions such as Africa, Oceania and South America [72]. More than 160 million tonnes of bauxite are mined each year [72].



Figure 9. The Al lifecycle [73].

The first step in producing AI is to crush the bauxite and purify it using the Bayer Process, where the bauxite is washed in a hot solution of sodium hydroxide (NaOH), which leaches AI from the bauxite. Typically, about 100 kg of caustic solution is consumed for each tonne of alumina produced [71]. AI is precipitated out of solution in the form of AI(OH) $_3$ [74]. AI(OH) $_3$ is then calcined to form alumina by heating in rotary kilns or fluidized bed calciners [74]. Due to the high energy requirement of rotary kilns, calciners are the preferred option which is based on the fluid-bed principle whereby the injected gas suspends the hydrate particles as they are carried through the calcining profile over a period of seconds [71]. The temperature applied is important, to ensure the desirable alumina product quality. At temperatures of 400-600 $^{\circ}$ C $_{7}$ -AI $_{2}$ O $_{3}$ forms which is chemically active. In order to produce smelting grade alumina (α -alumina) that is chemically inert, calcination is typically carried out at over 1000 $^{\circ}$ C [75]. The main impurity of calcined alumina obtained from the Bayer process is sodium oxide (Na $_{2}$ O) concentration of which may vary between 300 to 7000 ppm [71].

Figure 10 shows the different steps involved in the Bayer process. It takes roughly 4-7 tonnes of bauxite to produce 2 tonnes of alumina [76]. Typically, the Bayer process consumes about 12 GJ (3.3 MWh) energy per 1 tonnes of alumina produced out of which calcination alone accounts for 3.1 GJ/t (~0.9 MWh) [71, 77]. However, this will vary depending on the composition of the bauxite and size and efficiency of the plant. The details about the Bayer process can be found in the link below:

https://nzic.org.nz/app/uploads/2018/09/Bauxite-to-Alumina-Book-2018.pdf

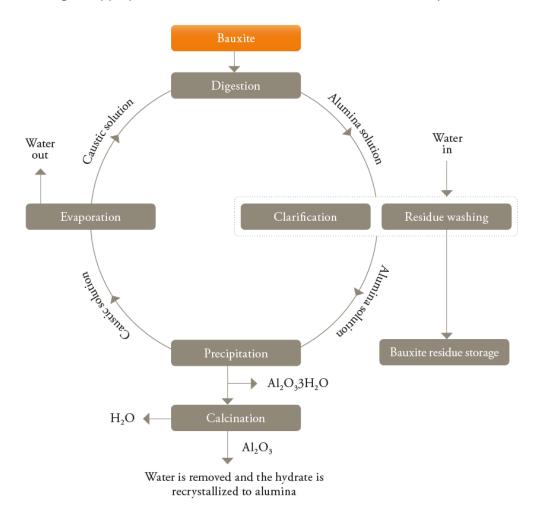


Figure 10. Simplified flow diagram for the Bayer process [76].

Al is smelted from the alumina via the Hall-Heroult process demonstrated in Figure 11. Alumina is dissolved in an electrolytic bath of molten cryolite (sodium aluminium fluoride, Na₃AlF₆) at temperatures around 950 °C within a large carbon or graphite lined steel container known as a "pot" [76]. An electric current of 200,000-500,000 A flows between the carbon anode (made of petroleum coke and pitch) and the cathode (formed by the thick carbon or graphite lining of the pot) [76]. The current passing through the alumina/bath solution reduces the alumina to Al and O₂. The molten Al is deposited at the cathode and is

siphoned off periodically [76]. Just under 2 tonnes of alumina are needed to produce 1 tonne of Al metal. The overall reaction is [71]:

$$2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$$
 Equation.4

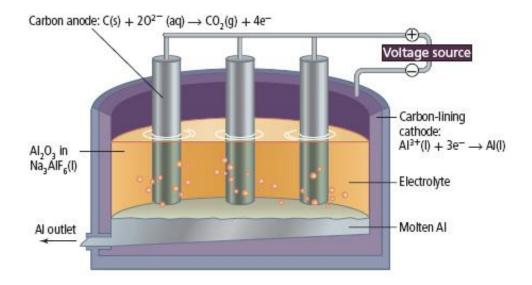


Figure 11. Illustration of the Hall-Heroult process.

Smelting of alumina to produce AI is an energy-intensive process, with a typical energy consumption of around 51 GJ (14.2 MWh) per tonnes of AI metal produced [71]. This number does not include the energy used in mining and transporting the ore, the energy for the Bayer process, or the energy used in casting or carbon plants [78]. Electricity consumption by the Hall-Heroult electrolytic process accounts for between 20 and 40 % of the cost of producing AI depending on local electricity cost [79]. In the United States, AI production consumes approximately 5 % of the total electricity generated.

Environmental issues related to primary Al production

There are several environmental concerns related to primary Al production. First, Bauxite mining involves disturbance of relatively large land areas as a result of its location close to the surface and relatively shallow thickness. On average one square meter of land is mined (including roads and infrastructure) in order to give one tonne of Al [76]. The annual worldwide encroachment on new land related to bauxite mining is about 40-50 km² [76]. Depending on the local circumstances, the mining operations may involve a number of environmental issues including [76]:

- removal and re-establishment of vegetation; change of landscape
- control of erosion and run off from the mine

- disturbance of hydrology
- waste disposal (tailings)
- mining operations and transport of bauxite including dusting and noise
- opening new areas may also provide access to illegal logging, farming, settling and hunting.

The main environmental issues associated with alumina production from the bauxite (the Bayer process) are [76]:

- disposal of the bauxite residue
- energy consumption and corresponding GHG emissions
- water management (process water as well as surface water from precipitation and run-off from the bauxite residue deposits needs to be cleaned before being discharged to the environment)
- physical footprint of the plant with infrastructure and the bauxite residue disposal area.

As mentioned above, smelting of alumina to produce AI (the Hall-Heroult electrolytic process) is very energy intensive leading to significant GHG emissions and energy costs unless the energy for this process is supplied by a means of renewable energy. Other environmental concerns associated with the Hall-Heroult process are [76]:

- emissions of fluoride, SO₂, dust and polycyclic aromatic hydrocarbon (PAH)
- liquid effluents
- waste disposal.

In 2016 nearly 59 million tonnes of primary AI were produced around the world, separate to secondary aluminium produced by recycling scrap metal [71]. Using the typical energy consumption figures stated above for the Bayer and Hall-Heroult processes, the estimated energy consumption per tonne of primary AI produced is about 17.5 MWh corresponding to total energy consumption of about 1,000,000 GWh in 2016. This does not include the energy usage by mining, delivery and other processes involved. According to the report from the World Resources Institute (WRI), GHG emissions associated with AI production account for approximately 0.8 % of global GHG emissions, which amounts to about 4 % of all manufacturing emissions [80]. To meet the increasing demand for AI, there is a continuous rise in its production, which is projected to increase to 89-122 Mt in 2050 [81].

5.2. Recycling of Al

Al recycling, also referred to as secondary Al production, involves collection and processing of Al-bearing scraps or materials followed by re-melting and refining [17]. Typically, Al materials (scrap or ingots) are washed to remove impurities and melted at 450-500 °C in a furnace (reverberatory, rotary and electric furnaces) [81]. The molten Al is then refined to produce Al followed by casting.

Al is infinitely recyclable meaning it is essentially unchanged no matter how many times it is processed and used [82]. The metal loss in the re-melting process is less than 3 % [76]. Around 75 % of the Al ever produced is still in use, and constitutes a resource bank for use in the future [9].

Recycling Al significantly reduces energy consumption, as it only requires about 5 % of the energy needed to produce the primary Al meaning 95 % of energy used for primary Al production can be saved [76, 83]. As a result, an equal amount of GHG emissions is saved each time an Al product is recycled at the end of its life [80, 82]. One tonne of recycled Al can save up to 8 tonnes of bauxite, 14,000 kWh of energy, 6300 litres of oil, 7.6 m³ of landfill, and the average total carbon emission is about 350 kg of CO₂ [84]. Today, recycling of post-consumer Al products saves over 90 million tonnes of CO₂ and over 100,000 GWh of electrical energy annually compared to primary production of the metal, equivalent to the annual power consumption of the Netherlands [74].

In addition to reduction in energy consumption and associated GHG emissions, increase in recycling of Al also [76, 83]:

- reduces amount of waste that needs to be buried or burned (Researches suggested that the mass of solid waste generated per tonne of secondary Al is 90 % lower than that of primary metal [80]).
- decreases mining requirement and related environmental and social impacts
- reduces the pollutants resulting from the primary Al production.

The successful recycling of Al depends on several factors including [85]:

- A plentiful and recurring supply of the metal, concentrated sufficiently in one area to justify the cost of collecting it.
- An infrastructure for collecting the scrap metal, removing impurities, and delivering it to a recycling facility.

- A method for recycling the metal that is economically competitive with the production of the metal from natural ores.
- A market for the recycled metal, should its composition or quality differ from that of primary metal.

Al can be recycled from a wide variety of scraps, originating from different Al alloys, with different alloying elements, in different amounts [84]. Al scrap is often categorized as "new scrap" and "old scrap". New scrap originates during the manufacturing of Al semi-fabricated and final products (e.g. shavings, off-cuts, molded parts, etc.) where the quality and composition are often known. Old scrap refers to those products collected after disposal from consumers, thus at the end of their life. Old scraps are more contaminated than new scraps and preliminary treatments of the scrap are usually necessary [84].

The main challenge in AI recycling is the chemical composition, as it is difficult to control the level of impurities and obtain the targeted alloy composition [84]. Casting alloys have higher AI content (up to 20 wt.%) than wrought ones, with the latter having a concentration of up to 10 wt. %. Therefore, the recycling process differs depending on the scrap properties. Remelters produce wrought alloys, usually in the form of extrusion billets and rolling ingots. Scraps for the production of wrought alloys should be sorted with a strict control of the concentration of alloying elements in order to achieve the prescribed compositional tolerances [86]. Well-defined wrought scrap of a proper composition can be effectively remelted into a wrought alloy of the same composition, but it is very challenging to obtain a new wrought composition with direct reuse, without an addition of the primary AI and alloying elements [86]. An addition of primary AI is necessary to dilute impurities (the elements not normally present in a wrought alloy) to an acceptable level, while the alloying elements are added, if necessary, for the correction of their concentration. Therefore, most of the external scrap inside the EU (above 60 %) is preferably applied in the production of casting alloys and only the remainder is dedicated to remelting [86].

Refiners produce casting alloys and deoxidation Al from scrap of varying composition; they mix these scrap types together, add alloying elements and remove certain unwanted elements after the melting process to produce alloys to customers specifications [87].

Table 3 gives the classification of different Al scraps, where the metal yield indicates the portion of a scrap consignment that becomes useable metal after proper melting.

Table 3. Classification of AI scrap showing the metal yields (lower limit and average value), the average amounts of undesired materials (oxides and foreign materials) and the cost. Data are read and elaborated from the different parts of EN 13920 standard [84].

EN 13920 Part No.	Scrap	Metal Yield Lower Limit (%)	Metal Yield Avg. Value (%)	Oxides (%)	Foreign Material (%)	Cost [24] * (€/ton)
2	unalloyed aluminum	0.95	-	-	-	1232-1332
3	wire and cable	≥0.95	97.7	1.3	0.5	1182-1282
4	single wrought alloy	≥0.95	97.2	1.8	1.8	1272-1377
5	two or more wrought alloys—same family	≥0.88	97.2	1.0	2.0	1172–1222
6	two or more wrought alloys	$\geq \! 0.88$	94.0	0.8	5.2	-
7	Casting	≥0.9	83.4	6.2	10.4	-
8	Shredded (not separated)	≥0.9	-	-	-	-
9	shredded (separated)	≥0.9	84.5	5.4	10.1	-
10	used beverage cans	$\geq \! 0.88$	94.0	0.8	5.2	770-820
11	Al-Cu radiators	-	-	-	-	2247-2297
12	Turnings single alloy	≥0.9	95.3	3.7	1.0	1192-1257
13	mixed turnings	≥0.9	84.0	3.3	12.8	1157-1207
14	coated packaging	≥0.28	71.5	3.8	24.7	-
15	de-coated packaging	_ ≥0.8	86.1	12.9	1	-
16	dross	≥0.3	55. <i>7</i>	44.3	-	158-338

^{*} Available data are referred to market quotation on October 2017.

6. Conclusion

This report has reviewed the potential H_2 markets for HOD systems proposed by PhusionH2. There is a growing hydrogen demand in industrial applications which dominate the existing hydrogen market at a share of 90 %. These markets include chemical industry such as ammonia and methanol production, refineries, fertilizer for agriculture, H_2 welding, metallurgy, glass, food processing, electronic industry, pharmaceuticals and utilities. H_2 is predominantly supplied to the industrial applications by the SMR process resulting in carbon emissions and dependence on methane supply. In addition, most of these applications rely on H_2 delivery unless H_2 is generated on-site. A low cost and low carbon solution to supply H_2 for the industrial applications can be attractive in both economic and environmental point of view.

A potential application for on-site H₂ production is the hydrogen-cooled generators where using H₂ as a coolant instead of air has several operational benefits. There are already many power plants in the UK and around the world that utilize hydrogen-cooled generators where on-site H₂ generation could reduce H₂ cost, avoid the safety concerns associated with the delivery of H₂ to the site and provide security of supply.

Future H₂ markets also rely on the implementation of FC systems including both mobile and stationary applications. As early markets, materials handling equipment and back-up power have great potential for the use of FC systems instead of the conventional methods. This provides significant operational advantages and potentially economic benefits. The penetration of the FC systems in the transport systems, on the other hand, mainly depends

on policies restricting GHG emissions and air pollution as well as reductions in the technology cost. It is projected that the penetration of H₂ vehicles will be in the region of 40-75 % by 2050. However, a wide network of HRSs has yet to be developed to meet the demand for increasing numbers of H₂ vehicles. In order to truly recognize the environmental benefits of H₂ as a fuel for vehicles, H₂ needs be supplied from a low carbon source with minimum indirect fuel emissions. Low cost on-site generation can help reduce H₂ cost and avoid the logistical, financial and safety issues associated with H₂ delivery. While the transition to H₂ vehicles is as a long term solution which can provide deep decarbonisation of the transport sector, blending H₂ with conventional fuels such as diesel could help reduce emissions from existing units as a short-term solution before the FC systems and HRSs become widely adopted.

Another potential application for H₂ generators is decarbonizing of heat, which is not dependant on the penetration of FC systems. H₂ seeks to replace natural gas, enabling deep decarbonisation of heat, whilst still utilising similar gas appliances. There are several projects run by network operators in partnership with industry, look at converting the grid from natural gas to H₂.

This report has also provided a brief overview of the potential markets for the by-products generated by PhusionH2 HOD systems, i.e. aluminium hydroxide or iron oxide. Aluminium hydroxide finds applications as the largest flame retardant at a share of 38 % of the global flame retardants market. It is also used as a smoke suppressant for a wide range of polymers, as well as being a feedstock to manufacture other Al compounds such as alumina. Alumina produced from aluminium hydroxide can find use in industrial applications including metal Al production, filler for plastics, substitute for industrial diamond spark plugs, tap washers, abrasion resistant tiles, and cutting tools. High purity alumina serves as a base material for the manufacture of sapphire substrates that are used in various applications such as scratch-resistant artificial sapphire glass (for smartphones and smart watches), LED lights, and semiconductor wafers.

Iron oxides are used as pigments for a wide range of applications including coatings, construction materials, colorants for ceramics, glass, paper, plastics, rubber and textiles. Iron oxides have been extensively used as catalysts in various heterogeneous catalytic processes, e.g. steam reforming. Other applications for iron oxides are biological and biomedical fields, magnetic separation for industrial water treatment, and development of materials for electromagnetic interference shielding.

The carbon footprint and cost of H₂ generated through HOD systems highly depend on the source of energy and feedstock used for the reaction. Production of recycled Al only requires about 5 % of the energy needed to manufacture the primary Al from bauxite ores, providing a significant energy reduction and corresponding decrease in the GHG emissions. In addition, recycling of Al eliminates mining requirements, pollutants and wastes associated with primary Al production. However, depending on the Al scrap properties, the recycling process varies and may require tight specifications. Utilization of secondary Al recycled from a cheap feedstock, using a renewable energy source, has a potential to produce low cost and low carbon hydrogen through HOD systems.

References

- 1. Acar, C. and I. Dincer, *Comparative assessment of hydrogen production methods from renewable and non-renewable sources.* International journal of hydrogen energy, 2014. **39**(1): p. 1-12.
- Dincer, I. and C. Acar, Review and evaluation of hydrogen production methods for better sustainability. International journal of hydrogen energy, 2015. 40(34): p. 11094-11111.
- 3. da Silva Veras, T., T.S. Mozer, and A. da Silva César, *Hydrogen: trends, production and characterization of the main process worldwide.* International journal of hydrogen energy, 2017. **42**(4): p. 2018-2033.
- 4. Edwards, P.P., et al., *Hydrogen and fuel cells: towards a sustainable energy future.* Energy policy, 2008. **36**(12): p. 4356-4362.
- 5. IEA. *Hydrogen production and Storage*. 2006 [cited 25th January 2017]; Available from: https://www.iea.org/publications/freepublications/publication/hydrogen.pdf.
- 6. Shell. Shell Hydrogen Study. 2017; Available from: https://www.shell.com/energy-and-innovation/the-energy-future/future-transport/hydrogen/jcr_content/par/textimage_1062121309.stream/1496312627865/46fec8302a3871b190fed35fa8c09e449f57bf73bdc35e0c8a34c8c5c53c5986/shell-h2-study-new.pdf.
- 7. IEA. Global Trends and Outlook for Hydrogen. 2017; Available from: http://ieahydrogen.org/pdfs/Global-Outlook-and-Trends-for-Hydrogen Dec2017 WEB.aspx.
- 8. Gupta, R.B., *Hydrogen fuel: production, transport, and storage*. 2008: Crc Press.
- 9. Ren21. Renewables 2018 Global Status Report. 2018; Available from: http://www.ren21.net/wp-content/uploads/2018/06/17-8652 GSR2018 FullReport web final .pdf.
- 10. Schlapbach, L. and A. Züttel, *Hydrogen-storage materials for mobile applications*. Nature, 2001. **414**(6861): p. 353-358.
- 11. Winter, C.-J., *Hydrogen energy—abundant, efficient, clean: a debate over the energy-system-of-change.* International journal of hydrogen energy, 2009. **34**(14): p. S1-S52.
- 12. Badwal, S., S. Giddey, and F. Ciacchi, *Hydrogen and oxygen generation with polymer electrolyte membrane (PEM)-based electrolytic technology.* Ionics, 2006. **12**(1): p. 7-14.
- 13. Lipman, T., An overview of hydrogen production and storage systems with renewable hydrogen case studies. Clean energy states Alliance, 2011. **32**.
- 14. Forsberg, C.W., *Hydrogen markets: implications for hydrogen production technologies.* International Journal of Hydrogen Energy, 2005.
- 15. Hydrogenics. *Hydrogen Technology Gets Traction*. 2013 [cited 26/02/2018; Available from: http://www.hydrogenics.com/wp-content/uploads/hydrogenics-presents-at-cleantech-forum.pdf?sfvrsn=0.
- 16. CertifHy. Overview of the market segmentation for hydrogen across potential customer groups, based on key application areas. 2015; Available from: https://www.fch.europa.eu/sites/default/files/project_results_and_deliverables/D%201_2.%20Overview%20of%20the%20market%20segmenatation%20for%20hydrogen%20across%20potential%20customer%20groups%20based%20on%20key%20application%20areas.pdf.
- 17. Siemens. "Green" ammonia is the key to meeting the twin challenges of the 21st century. 2017; Available from: http://www.siemens.co.uk/en/insights/potential-of-green-ammonia-as-fertiliser-and-electricity-storage.htm.
- 18. IEA. Technology Roadmap Energy and GHG Reductions in the Chemical Industry via Catalytic Processes. 2013; Available from:

- https://www.iea.org/publications/freepublications/publication/TechnologyRoadmapEnergyandGHGReductionsintheChemicalIndustryviaCatalyticProcesses.pdf.
- 19. Revolvy. *Hydrogen-cooled turbo generator*. 2018; Available from: https://www.revolvy.com/page/Hydrogen%252Dcooled-turbo-generator.
- 20. AZO. *Cooling Generators with Hydrogen*. 2017; Available from: https://www.azom.com/article.aspx?ArticleID=14630.
- 21. PersistenceMarketResearch. *Hydrogen Cooled Generators Market: Global Industry Trend Analysis 2012 to 2017 and Forecast 2017 2025.* 2018; Available from: https://www.persistencemarketresearch.com/market-research/hydrogen-cooled-generators-market.asp.
- 22. HyLIFT. *HyLIFT-EUROPE project for materials handling*. 2018; Available from: http://www.hylift-europe.eu/index.html.
- 23. NREL. *Early Markets: Fuel Cells for Material Handling Equipment*. 2007; Available from: https://www.nrel.gov/docs/fy07osti/41571.pdf.
- 24. AirProducts. *Material Handling*. 2018; Available from: http://www.airproducts.co.uk/Industries/Energy/Hydrogen-Energy/Material-Handling.aspx.
- 25. Ballard. *Economics of Fuel Cell Solutions for Material Handling*. 2010; Available from: http://ballard.com/docs/default-source/motive-modules-documents/material-handling/mh econbenefits fcvelocity 041411.pdf?sfvrsn=2.
- 26. HYLIFT. Fuel Cell Materials Handling Vehicle Market Developments in Europe 2018; Available from: http://www.hylift-europe.eu/public/Presentations/2018_03_14_HyLIFT-Europe-EEVC CristinaMaggi.pdf.
- 27. FCH. Development of Business Cases for Fuel Cells and Hydrogen Applications for Regions and Cities. 2017; Available from: https://www.fch.europa.eu/sites/default/files/FCH%20Docs/171121_FCH2JU_Application-package_WG2_Material%20handling%20equipment%20%28ID%202910567%29%20%28ID%202911653%29.pdf.
- 28. Renquist, J.V., B. Dickman, and T.H. Bradley, *Economic comparison of fuel cell powered forklifts to battery powered forklifts.* international journal of hydrogen energy, 2012. **37**(17): p. 12054-12059.
- 29. Hydrogenics. *Telecon and Data Centre Backup Power*. 2019; Available from: https://www.hydrogenics.com/hydrogen-products-solutions/fuel-cell-power-systems/stationary-stand-by-power/telecom-data-centre-backup-power/.
- 30. Serincan, M.F., *Reliability considerations of a fuel cell backup power system for telecom applications.* Journal of Power Sources, 2016. **309**: p. 66-75.
- 31. NREL. *Early Markets: Fuel Cells for Backup Power*. 2007; Available from: https://www.nrel.gov/docs/fy07osti/41572.pdf.
- 32. Barbir, F. *Fuel Cells Applications, Backup Power.* 2013; Available from: https://www.sciencedirect.com/topics/engineering/back-up-power.
- 33. NREL, Fuel Cell Backup Power Unit Configuration and Electricity Market Participation: A Feasibility Study. 2017.
- 34. EEA. *Transport*. 2018; Available from: https://www.eea.europa.eu/themes/transport.
- 35. EEA. *Greenhouse gas emissions from transport*. 2018; Available from: https://www.eea.europa.eu/data-and-maps/indicators/transport-emissions-of-greenhouse-gases-11.
- 36. BEIS. Energy Consumption in the UK. 2018; Available from:

 https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/729317/Energy_Consumption_in_the_UK_ECUK_2018.pdf.
- 37. BEIS. 2017 UK Greenhouse Gas Emissions, Provisional Figures. 2018; Available from:

- https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/695930/2017_Provisional_Emissions_statistics_2.pdf.
- 38. UKGOV. *Transport Statistics Great Britain 2017*. 2018; Available from: https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachm ent_data/file/664323/tsgb-2017-print-ready-version.pdf.
- 39. Singh, S., et al., *Hydrogen: A sustainable fuel for future of the transport sector.* Renewable and Sustainable Energy Reviews, 2015. **51**: p. 623-633.
- 40. PolicyExchange. *Driving Down Emissions* 2017; Available from: https://policyexchange.org.uk/wp-content/uploads/2017/06/Driving-down-emissions-How-to-clean-up-road-transport.pdf.
- 41. FCH. Fuel Cells and Hydrogen Joint Undertaking (FCH JU) Multi Annual Work Plan. 2014; Available from:

 https://www.fch.europa.eu/sites/default/files/documents/FCH2%20JU%20-%20Multi%20Annual%20Work%20Plan%20-%20MAWP en 0.pdf.
- 42. HyWays. *The European Hydrogen Energy Roadmap*. Available from: https://www.ecn.nl/publications/PdfFetch.aspx?nr=ECN-B--08-006.
- 43. E4Tech. *Hydrogen Refuelling & Storage Infrastructure*. Available from: http://www.hi-energy.org.uk/Downloads/Hydrogen%20Fuel%20Cell%20Resource/3b-Hydrogen%20refuelling%20and%20storage%20infrastructure.pdf.
- 44. EESI. *A portfolio of power-trains for Europe: a fact-based analysis*. Available from: https://www.eesi.org/files/europe_vehicles.pdf.
- 45. TheLindaGroup. *Production and Utilization of Green Hydrogen*. 2012; Available from: https://www.wko.at/site/OEGEW/Veranstaltungen/Herbsttagung-2012-Vortrag-04-Korobov.pdf.
- 46. Parliament. *Decarbonising the Gas Network*. 2017; Available from: https://researchbriefings.parliament.uk/ResearchBriefing/Summary/POST-PN-0565#fullreport.
- 47. Joshi, N. and D. Naik, *Onboard production of hydrogen gas for power generation.* Journal of Research in Mechanical Engineering, 2015. **2**: p. 1-11.
- 48. Köse, H. and M. Ciniviz, *An experimental investigation of effect on diesel engine performance and exhaust emissions of addition at dual fuel mode of hydrogen.* Fuel processing technology, 2013. **114**: p. 26-34.
- 49. Bari, S. and M.M. Esmaeil, *Effect of H2/O2 addition in increasing the thermal efficiency of a diesel engine*. Fuel, 2010. **89**(2): p. 378-383.
- 50. The Engineer. *UK's first marine hydrogen injection system funded for Orkney ferry*. 2018; Available from: https://www.theengineer.co.uk/hydrogen-diesel-injection-orkney-ferry/.
- 51. UKResearchandInnovation. *HyDIME (Hydrogen & Diesel Injection in a Marine Environment)*. 2018; Available from: https://gtr.ukri.org/projects?ref=104366.
- 52. IHSMarkit. *Flame Retardants*. 2017; Available from: https://ihsmarkit.com/products/chemical-flame-retardants-scup.html.
- 53. Huber. *Non-halogen fire retardant additives*. 2018; Available from: https://www.hubermaterials.com/userfiles/files/PFDocs/Huber%20Non-Halogen%20Fire%20Retardant%20Additives.pdf.
- 54. Hull, T.R., A. Witkowski, and L. Hollingbery, *Fire retardant action of mineral fillers*. Polymer degradation and stability, 2011. **96**(8): p. 1462-1469.
- 55. DataMIntelligent. Global Flame Retardants Market Size, Share and Forecast (2018 2025). 2018; Available from: https://www.datamintelligence.com/research-report/flame-retardants-market/?gclid=EAlalQobChMl69qi7_vd3wlVhZztCh3pBQ7sEAAYAiAAEgLsy_D_Bw_F
- 56. Flameretardants. *The flame retardants market*. 2018; Available from: https://www.flameretardants-online.com/flame-retardants/market.

- 57. Evans, K., *Properties and uses of aluminium oxides and aluminium hydroxides*. The Chemistry of Aluminium, Indium and Gallium, ed. AJ Downs, Published by Blackie Academic, 1993.
- 58. NCBI. *Aluminum Hydroxide*. Available from: https://www.ncbi.nlm.nih.gov/mesh/68000536.
- 59. Potter, M.J. *Iron oxide pigments*. 2014; Available from: https://minerals.usgs.gov/minerals/pubs/commodity/iron_oxide/750494.pdf.
- 60. NSW. *Iron oxide pigments*. Available from: https://resourcesandgeoscience.nsw.gov.au/_data/assets/pdf_file/0006/237849/Iron oxide.pdf.
- 61. FutureMarketInsights. Iron Oxide Market; Paints and Coating to Surface as New Avenue for Iron Oxide Producer and Support Demand for the same over the Forecast Period: Global Industry Analysis and Opportunity Assessment, 2015 2025. 2016; Available from: https://www.futuremarketinsights.com/reports/iron-oxide-market.
- 62. Soares, B., Rubber nanocomposites with metal oxides as nanofillers, in Progress in Rubber Nanocomposites. 2017, Elsevier. p. 285-318.
- 63. IronPowder. *Black Iron Oxide*. 2019; Available from: https://www.iron-powder.com/black-iron-oxide/.
- 64. Pereira, M., L. Oliveira, and E. Murad, *Iron oxide catalysts: Fenton and Fentonlike reactions—a review.* Clay Minerals, 2012. **47**(3): p. 285-302.
- 65. Barbini, R., et al., *Application of laser-induced breakdown spectroscopy to the analysis of metals in soils.* Applied Physics A, 1999. **69**(1): p. S175-S178.
- 66. Sigma-Aldrich. *Iron Oxide Nanoparticles, Characteristics and Applications*. 2019; Available from: https://www.sigmaaldrich.com/technical-documents/articles/technology-spotlights/iron-oxide-nanoparticles-characteristics-and-applications.html.
- 67. FutureMarketInsights. Global Iron Oxide Market is expected to register a CAGR of 4.3% in terms of value during 2015–2025 and Primary Iron Oxide Type is pegged to be the Dominant Segment in the Market. 2016; Available from: https://www.futuremarketinsights.com/press-release/iron-oxide-market.
- 68. AZO. Alumina (Aluminium Oxide) The Different Types of Commercially Available Grades. 2002; Available from: Alumina (Aluminium Oxide) The Different Types of Commercially Available Grades.
- 69. AluminumAssociation. *Alumina Refining*. 2019; Available from: https://www.aluminum.org/industries/production/alumina-refining.
- 70. PersistenceMarketResearch. Global Market Study on High Purity Alumina (HPA): High Demand for LED's and Displays to Drive Growth During 2015-2021. 2016; Available from: https://www.persistencemarketresearch.com/market-research/high-purity-alumina-market.asp.
- 71. Bagshaw, A.N. *The Aluminium Story Bauxide to Alumina: The Bayer Process.* 2017; Available from: https://nzic.org.nz/app/uploads/2018/09/Bauxite-to-Alumina-Book-2018.pdf.
- 72. AluminumAssociation. *Bauxite*. 2019; Available from: https://www.aluminum.org/industries/production/bauxite.
- 73. Hulamin. *Aluminium's Lifecycle*. 2018; Available from: https://www.hulamin.com/about/aluminiums-lifecycle.
- 74. King, H.M. *Bauxite*. 2019; Available from: https://geology.com/minerals/bauxite.shtml.
- 75. Lamouri, S., et al., Control of the γ-alumina to α-alumina phase transformation for an optimized alumina densification. Boletín de la sociedad española de cerámica y vidrio, 2017. **56**(2): p. 47-54.
- 76. Hydro. *Aluminium environment and society*. 2012; Available from: https://www.hydro.com/globalassets/1-english/about-aluminium/files/aluminium_environment-and-society.pdf.

- 77. Mahadevan, H. and T. Ramachandran, *Recent trends in alumina and aluminium production technology.* Bulletin of Materials Science, 1996. **19**(6): p. 905-920.
- 78. DOE. Reaction of Aluminum with Water to Produce Hydrogen. 2008; Available from: https://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/aluminium_water_hydrogen.pdf.
- 79. AluminumAssociation, Primary Production. 2018.
- 80. Jirang, C. and H.J. Roven, *Recycling of automotive aluminum*. Transactions of Nonferrous Metals Society of China, 2010. **20**(11): p. 2057-2063.
- 81. Gautam, M., B. Pandey, and M. Agrawal, *Carbon Footprint of Aluminum Production: Emissions and Mitigation*, in *Environmental Carbon Footprints*. 2018, Elsevier. p. 197-228.
- 82. EuropeanAluminium, Recycling Aluminum A pathway to a Sustainable Economy. 2015.
- 83. Husband, T. *Recycling aluminium*. 2012; Available from: https://www.acs.org/content/dam/acsorg/education/resources/highschool/chemmatters/archive/aluminum-recycling-chemmatters-april-2012.pdf.
- 84. Capuzzi, S. and G. Timelli, *Preparation and Melting of Scrap in Aluminum Recycling: A Review.* Metals, 2018. **8**(4): p. 249.
- 85. Schlesinger, M.E., *Aluminum recycling*. 2013: CRC press.
- 86. IZ, R.G.A.Z., Challenges and advantages of recycling wrought aluminium alloys from lower grades of metallurgically clean scrap. Materiali in tehnologije, 2013. **47**(1): p. 13-23.
- 87. ALU. *Industry Structure*. 2018; Available from: http://recycling.world-aluminium.org/review/industry-structure/.

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