

Hydrogen Exploitation on Extractive Industry Oriented to Green Electrification and Heat Production

Antonis Peppas¹, Chrysa Politi², Sotirios Kottaridis³, Lampros Karalis⁴,
Panagiotis Angelopoulos⁵ and Maria Taxiarchou⁶

1. Assistant Professor
2. Junior Researcher
3. Junior Researcher
4. Senior Researcher
5. Senior Researcher
6. Associate Professor

School of Mining and Metallurgical Engineering, National Technical University of Athens
(NTUA), Athens, Greece

Corresponding author: peppas@metal.ntua.gr

Abstract

With an annual global CO₂ emission of 34 billion tonnes due to fossil fuel usage, the need for a worldwide gradual decarbonisation plan is urgent. To meet the environmental milestones of 2050, the world needs to contribute an annual 6 % decrease in fossil fuel use, accounting for 73 % of global CO₂ emissions. For achieving these goals, Energy Intensive Industries should examine establishing alternative energy supply routes and circular system processes to minimise the need for fossil fuel external energy sources, wastes etc. Hydrogen is widely used in Extractive Industries as a reduction agent for numerous metal oxides, such as iron or cobalt, producing metal with improved environmental footprint. In the aluminium industry, the H₂ reduction is not applicable till now, mainly due to the need for very high temperatures and energy demands required for the reduction process. However, H₂ shows great potential as a very efficient and environmentally beneficial fuel for heat and electricity cogeneration, which can also be easily produced inside the aluminium production and process line. Additionally, the innovation potential for exploiting H₂ for the reduction of primary aluminium production wastes, such as bauxite residues enables their valorisation of wastes transforming them into high added value materials. This paper aims on reporting state-of-the-art H₂-based technologies for green electrification and medium / high-grade heat production and proposes a utilisation scheme for secondary aluminium smelting, presenting also the environmental advantages in comparison with conventional fossil fuel-based technologies. The proposed scheme enables a reduction of 49 %, 81 % and 61 % in global warming potential, acidification potential and photochemical oxidant formation respectively.

Keywords: Extractive industry decarbonisation, Green electrification, Medium / high grade heat production, Hydrogen, Aluminium.

1. Introduction

During the last decades, the world has taken a turn towards climate-neutral practices for the facilitation of environmental goals. To limit the global temperature rise by 1.5 °C, in line with the Paris Agreement, the world must contribute to a roughly 6 % annual reduction of fossil fuels, including coal, oil and gas. All coal-fired power stations will cease operations by 2040 at the latest [1]. With such industries making up more than half of the energy consumption in the EU, Energy Intensive Industries (EIIs) are responsible for 15 % of the EU's emissions [2]. These emissions are expected to significantly increase as the demand and needs of major EIIs (i.e., Extractive industries), see a constant rise.

In 2017, extraction of materials reached 92 billion tonnes in comparison with the 27 billion in 1970. If this trend continues, the annual global demand will reach 190 billion tonnes of material by 2060 [1]. More specifically, with the expected population and economic growth over the coming decades, global steel demand is expected to increase by approximately 30 %, while the demand for cement will be increased by 10 % and aluminium (Al) by about 75 % until 2060 compared to 2017 levels [3]. Despite the severe effects of Covid-19 on global markets, primary Al production in 2020 increased by 2.3 % to 65.3 million tonnes, and global Al demand was 98 million tonnes with recycling [4].

This rise in global demand consequently exacerbates the environmental challenge. The extraction and primary processing of metals and minerals accounted for 26 % of the Global Greenhouse Gas (GHG) emissions and 20 % of health impacts in 2019 [5, 6]. In 2021, the metals and mining sector was estimated to emit around 4.5 Gt of CO₂ equivalent per year [7]. Al in particular appears to be the most EII and the most CO₂-emissive. The high emissions are the result of fossil fuel usage. For that matter, an extensive investigation of the potential reduction of GHG emissions through fossil fuel use reduction is taking place, concerning the electrification of energy-intensive processes. Electrification is particularly challenging for fossil resources not used as energy supply but as feedstock. Replacing fossil fuels with electricity is not always directly possible since fossil fuels serve two use cases in EII: 1) supply of process heat by combustion and 2) use as a chemical feedstock. As such process heat demands are typically large, there is a limited number of alternatives to fossil fuels that can provide the required consistency, high temperatures and fluxes, thus making the minimization of fossil fuel need even more important.

Europe has historically a strong presence in metallurgy, representing about 7 % of the global production, around half of which comes from within the EU28, deploying more than 15 smelters, of which two were idled in 2019, and 600 Al production plants ranging from raw materials (e.g., bauxite and alumina), primary metal production, semi-fabrication (e.g rolling and extrusion), and recycling. In this regard, melting and heat treatment furnaces are widely used in the Al industry [8]. These furnaces have burners that are used with fossil fuels. Therefore, developing retrofitting solutions for existing infrastructure is a key enabler for the implementation of the H₂ technologies. With relatively small modifications to existing combustors, co-firing of H₂ can be allowed to significant fractions (>30 % vol., 11 % of C reduction) [9]. Overall, over half of our Europe's Al smelters have been affected by the power crises in the course of 2022. according to Eurométaux, the EU has temporarily lost 650 000 tonnes of primary Al capacity: about 30 % of its total. [10] Due to all these needs, the investigation of clean energy technologies is vital to ensure the adaptation of sustainable and responsible practices from the extractive industries as to meet the rising mineral demands up to 2050.

The main challenges are faced from secondary Al production which is a process of recycling Al scrap into ingots. Al recycling not only reduces the wastes that would otherwise be disposed, but also minimises the need for processes, such as alumina reduction for the primary Al production, making the production 95 % more energy efficient [11]. During secondary Al smelting, the scrap is extracted from wastes and then fed to the smelter to be melt at temperatures higher than 700 °C [11]. The main component of a secondary Al smelter is the furnace, in which the Al scrap is placed to be heated beyond its melting point by high-grade heat provided by fuels combustion through burners. In some cases, the required heat is provided by electricity or other energy sources. In addition, pre-heating of the material is required in order to remove moisture, prevent explosions in the furnace and reduce melting energy requirements [12]. After the smelting process, molten Al is transported to holding furnaces in the cast house to be turned into ingots [12].

2. H₂ Decarbonisation Routes for Extractive Industries

Hydrogen (H₂) presents a solution that sees a constant rise in use in the industry. It is estimated that by 2030 the first large-scale projects could pioneer the use of H₂, accounting for a total of 4 Mt, abating the rough equivalent of more than 10 million diesel cars [13]. By 2050, H₂ could meet about 12 % of final industrial energy demand (16 exajoule -EJ), providing up to 23 % of high-grade heat, 8 % of medium-grade heat, and 4 % of low-grade heat [13]. In Extractive industries specifically, H₂ shows much potential as a reduction agent for usable material extraction and as a fuel for combined heat and power (CHP).

For the minimisation of GHG emissions, metallurgical industries aim for reducing their fossil fuel needs, through waste exploitation and material recycling. Such approaches have found commercial success for different metals, such as platinum group metals, some rare metals like germanium and rhenium, as well as the production of special grades of metals (i.e., fine nickel and cobalt powders) [14]. Also, H₂ is especially efficient when it comes to the synthesis of tungsten and molybdenum with very pure powders as a result of the reduction of the oxides [14]. For iron oxides, H₂ is a much preferable reduction agent than CO, due to the reaction's better kinetic behaviour [15]. In case of Al, the utilisation of H₂ for oxides reduction is limited due to the high temperatures needed and contamination of the liquid metal with dissolved H₂. Nevertheless, for Extractive Industry of Al, H₂ provides an attractive alternative decarbonisation route to be utilised as a fuel, since it is clean, non-toxic and renewable.

2.1 H₂ as a Fuel for Green Electricity and Heat

Hydrogen fuel is a zero-carbon fuel burned with O₂, given that it was produced in a process that does not involve carbon (green H₂). It can be used in fuel cells or internal combustion engines to provide medium / high grade CHP. Indicatively, it has a lower heating value (LHV) of 120 kJ/kg in comparison with the 47.1 kJ/kg of natural gas (NG) [16]. Environmentally, the absence of carbon from the H₂ combustion results in zero CO₂ or CO emissions in comparison to the NG combustion [17], while it can result in emissions reduction by 65 % for dual-fuel Internal Combustion Engines (ICE), 98 % for mono-fuel ICE and up to 100 % reduction for fuel cells [18]. (Figure 1)

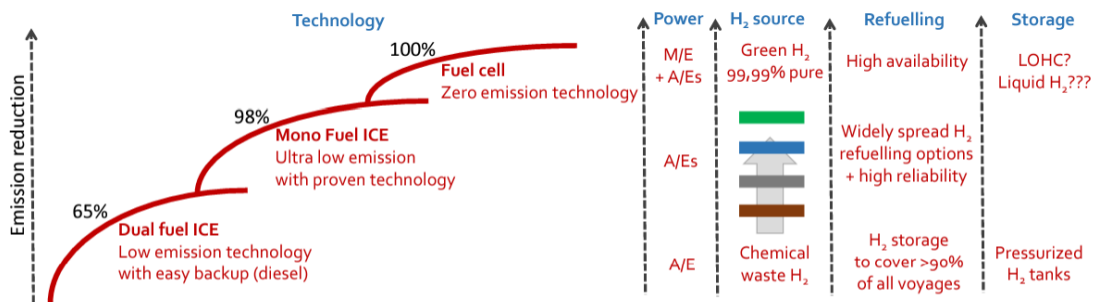


Figure 1. H₂-based technologies.

2.1.1 H₂-Fuelled SOFC

Solid oxide fuel cell (SOFC) is an electrochemical conversion device that produces electricity directly from oxidizing a fuel. In addition, SOFC power systems can increase their efficiency by using the heat given off by the exothermic electrochemical oxidation within the fuel cell for endothermic steam reforming process. For this reason, SOFCs are utilised for a wide variety of applications, from use as auxiliary power units in vehicles to stationary power generation with outputs from 100 W to 2 MW. Advantages of this class of fuel cells include high CHP efficiency,

long-term stability, fuel flexibility, low emissions, and relatively low cost. In addition, SOFC account for substantially lower < 0.5 ppm NO_x emissions in comparison with combustion-based electrical generation technologies [19].

H_2 is a good candidate for utilisation in fuel cell systems due to its high electrochemical activity. Additionally, the high operational temperatures allow for the internal reform of hydrocarbon fuels to H_2 [20]. On an industrial scale, SOFC systems utilising mixtures of H_2 and CO reacting with air's O_2 , have achieved net efficiencies of 55 %, combined heat efficiencies of 65 % or 73 % for recovered steam or hot water respectively, and CO_2 emissions reduction by around 47 % [21, 22]. It is also noteworthy that SOFC systems can operate in reverse mode as electrolyzers for electrolysing water to H_2 of almost 100 % efficiency.

2.1.2 H_2 Combustion

Hydrogen has a wide flammability range in comparison with other fuels enabling its use in an ICE over a wide range of fuel-air mixtures. An advantage here is it can thus be on a lean fuel-air mixture. Common technologies include the hydrogen–NG blends, the Diesel Dual Fuel (DDF) and the Hydrogen Mono Fuel (HMF) engines.

2.1.2.1 Hydrogen–NG Blends Engines

Using blends of H_2 with compressed NG (HCNG, H_2CNG , and Hythane®) in ICEs has proven valuable to improve thermal efficiency and to produce less noxious emissions. [23] Blending H_2 with NG is an effective solution to produce CHP without requiring extended modifications of the existing facilities and simultaneously achieving greater efficiency in power production under electrical energy surplus occurrence. [24] The admixture of H_2 into NG (which mostly consists of methane, CH_4) changes the properties of the fuel mixture as the two fuels differ significantly in their physical properties. These changes can lead to higher combustion temperatures and laminar combustion velocities, depending on the combustion system, burner design and other boundary conditions. As the level of H_2 increases at a fixed engine operative point, the in-cylinder temperature raises accordingly, while the combustion duration reduces, leading to lower unburned hydrocarbons (UHC) and CO emissions, but in augmented NO_x emissions [25].

2.1.2.2 Diesel Dual Fuel Engines

DDF combustion technologies utilise two different fuels, one as the main one and the other as an igniter. During DDF operation, H_2 is injected, mixed with intake gas and the pre-mixed gas is introduced to the combustion chamber. After compression and before its completion, diesel fuel is directly injected into the chamber for initializing the combustion process due to its self-ignition characteristics. A particular investigation of the effect of H_2 in DDF engines including the performance and emissions, has been performed by Karagöz et al. [26]. In this study, H_2 was introduced into the intake manifold using gas injectors as additive fuel in gaseous form and diesel fuel was injected into the cylinder by a diesel injector and used as the igniter. The study showed that the higher the H_2 fraction, the more significant the decrease in smoke, CO and CO_2 emissions, while an increase was observed in unburnt hydrocarbons and NO_x . The NO_x increase is due to the high flame temperature facilitating its formation. The main approach for minimising the NO_x emissions is keeping the flame temperature below the NO_x formation critical 1350 °C, by calibrating the fuel and air mixing rate [27].

2.1.2.3 Hydrogen Mono Fuel Engines

Hydrogen combustion engines can leverage existing technologies and provide a zero-emission option for specific use cases while supporting the growth of H_2 infrastructure. When focusing on

an HMF engine, H₂ is injected into the intake port mixing with air during induction stroke. On the ICEs, the inherent flammability of H₂ allows a very lean combustion, leading to zero or near-zero emission, depending on mixture ratio and load. In terms of air / fuel (A/F) ratios, HMF engines can operate on air/fuel (A/F) ratios of anywhere from 34:1 (stoichiometric) to 180:1. Operating the engine at ultra-lean conditions (A/F ≥ 68:1), NO_x emissions below 100 ppm could be achieved without using any after-treatment. In addition, the lean operation is contributing also to heat loss reduction [28]. The advantages of HMF compared to the fuel cell technology include a higher tolerance to fuel impurities, flexibility to switching fuels as well as the reduction of rare materials usage and consequently significant reductions in costs [29].

2.1.2.4 New Technologies Ready-to-Apply for Hydrogen Adaptation

Despite the high number of studies, there are still open challenges in H₂ technologies adaptation, including the determination of the proper H₂ fraction allowable to avoid rapid pressure rises and the definition of the optimal combination between the H₂ addition, the excess air ratio, and spark timing [30, 31]. Therefore, technologies ready-to-use are introduced aiming for faster and more efficient adaptation of H₂ technologies by industries.

Oxygen-enriched combustion is one of the latest technologies that may improve combustion efficiency depending on the exhaust gas temperature and percentage of oxygen in the combustion air [32]. O₂ is required any combustion process (NG, DDF, HMF), while the ambient air being the most common source, contains only about 21 % by volume. The rest 79 % of N₂ is inert gas and does not contribute in heat released through combustion reaction. O₂ enrichment (also known as increased O₂ %) can improve the overall combustion process and result in higher flame temperature and available heat. This is achieved as it increases the specific fuel rates in kg fuel/kg air (supplemental enrichment) and reduces the overall air volume (equivalent enrichment). Jun Li et. al. in their work investigated the different temperatures and heat release rates for different H₂ and O₂ ratios in a biogas fuel stream [33]. It was concluded the enrichment of the stream with O₂ was beneficial, with an increase in the O₂ ratio from 21 % to 35 % leading to an 11.2 % increase in temperature. Additionally, the maximum heat release rates were bigger by 3.69 times and 2.29 times respectively [33].

H₂ can be also utilised for bauxite residues reduction for the formation of magnetite that can be recovered by magnetic separation. Bauxite residue is the main Al industry waste generated during the treatment of bauxitic ores by sodium hydroxide (Bayer process) for producing alumina. Producing one tonne of alumina results in 1–1.5 t of bauxite residue with an estimated global annual production of 120 Mt [34, 35]. Such volumes of waste constitute an issue for the sustainability of the Al industries in both economic and environmental terms. M. Samouhos et al investigated the reduction and separation of iron oxide phases by H₂ gas reduction [35]. The results showed that the maximum conversion degree of hematite to magnetite was above 87 % conversion at 480 °C using 2.5 times stoichiometric H₂ supply. In addition to that, the wet magnetic separation showed that iron oxide phase separation is possible to a significant extent with a separation yield higher than the magnetic separation yield performed on raw red mud or after its reductive smelting.

The retrofitting of existing infrastructure (i.e., steel pipelines) can reduce the cost of H₂ utilisation in the industry. H₂ embrittlement is a major concern for scientists and gas installation designers to avoid process failures. It can be defined as the H₂-caused deterioration of the mechanical properties of most metallic materials and alloys. Various solutions to protect steel surfaces from H₂ absorption and diffusion include paint, and bulk materials doping coatings. Such approaches are widely proposed as an efficient solution to design H₂ barriers in order to trap the adsorbed H₂ atoms, and then avoid their diffusion towards the substrate through the interface [36]. Hard metallic (such as nickel superalloys, niobium or chromium-rich layer) or mixed metallic-ceramic

coatings enriched with TiN / TiC prepared by laser cladding also represent a promising alternative for the protection of steel metallic structures against H₂ embrittlement and corrosion degradation [37]. It is a technique that allows for the deposition of thick protective coatings on low-cost substrates. A high-power laser is used as the heat source that superficially melts the substrate, enabling the bonding with the coat[38]. The resulting thickness of the clad is typically 50 µm to 2 mm in a single step [39]. This way, high-quality clads whose overlapping produces layers that could be used to reinforce certain areas requiring special properties are generated.

3. H₂ Technologies Adaptation for Secondary Aluminium Smelting: Current Practice and Utilisation Scheme Comparative Life Cycle Assessment

3.1 Life Cycle Assessment Methodology

For the assessment of the environmental impact of the H₂ technologies and their integration into a secondary Al smelting plant, a Life Cycle Assessment (LCA) was performed by following the standardized procedures, as described by ISO 14040:2006 and 14044:2006/A1:2018, and the International Life Cycle Data (ILCD) Handbook [40-42]. The principles and framework of the LCA include the definition of goal and scope, the preparation of the Life Cycle Inventory (LCI), the life cycle impact assessment (LCIA), and the interpretation of the assessment results. In this study, a life cycle assessment is performed for a Secondary Aluminium smelting plant with the commercial software package GaBi 8.5, Sphera™ [43].

3.2 Scope Definition and Functional Unit Selection

An LCA is conducted comparing an utilisation scheme of H₂ technologies with the current practice (NG –based). Scope of this LCA analysis is to examine the energy and material flows within a secondary Al smelting plant and validate the green nature of the H₂-based CHP technologies (e.g., SOFC, H₂ ICE, etc.) in comparison to the conventional CHP production (NG burner). Thus, the Functional Unit (FU) is selected as 1 tonne of secondary aluminium ingot produced at the plant.

3.3 Scenarios Description and System Boundaries Definition

For the current analysis, the LCA two scenarios were selected based on the electricity and heat supply at the secondary Al smelter:

- Scenario 1 (NG): Thermal energy is provided by NG combustion (current practice) and electricity is provided by renewable energy sources (RES) systems;
- Scenario 2 (H₂): Thermal energy and electricity is provided by H₂ systems

The system boundaries included all the processes in the techno-sphere of the FU.

For scenario 1, NG is supplied from a process plant and transported to the secondary Al smelter for combustion in an industrial burner. For the NG transport, trucks and trains are used. The electricity demand for the operation of the smelter is provided by photovoltaics. Lastly, an Al recovery process is introduced for supplying the smelter with Al scrap. The current practice processes and the system boundaries are shown in Figure 2.

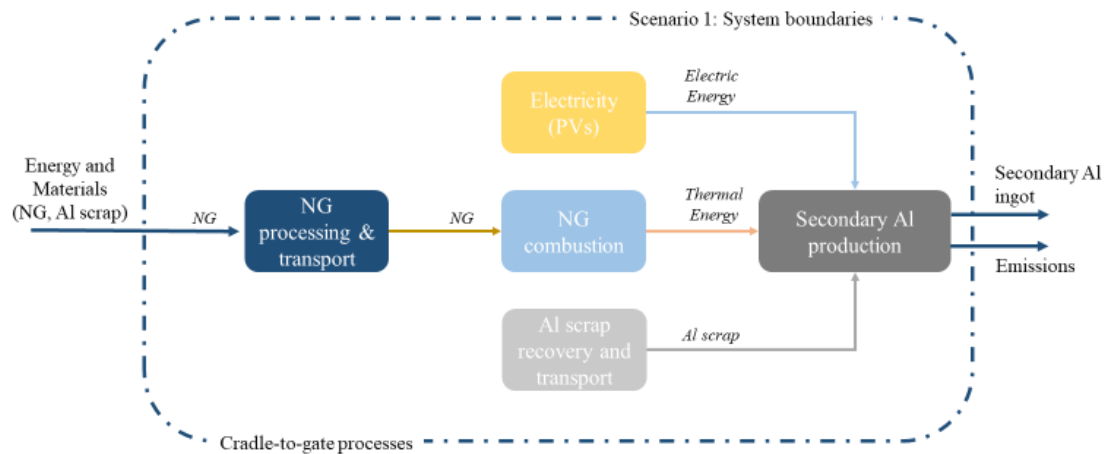


Figure 2. Scenario 1 system boundaries.

Scenario 2 uses H₂ for the production of both the required heat and electricity for the smelter. In this scenario, a H₂ SOFC supplies high-grade heat to the smelter, while also covering the electric demand of the smelter. The rest of the high-grade heat is supplied by an H₂ burner. Complimenting the SOFC technology, a H₂ ICE is utilised, providing the SOFC with the required electricity for operation, while also covering the medium-grade heat required for preheating the Al scrap. Lastly, the Al scrap recovery and transport process used for the supply of Al scrap is equivalent to the Scenario 1 process. The H₂ utilisation scheme and system boundaries are shown in Figure 3.

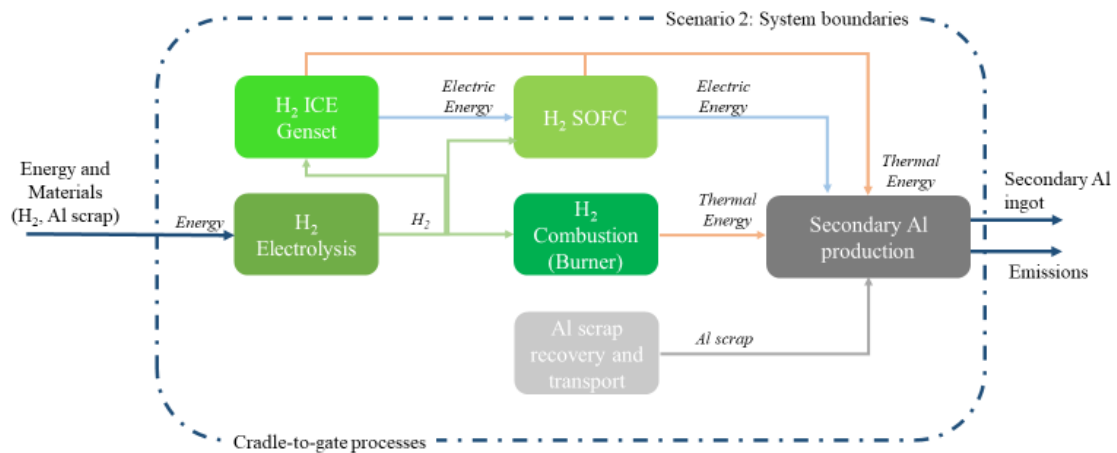


Figure 3. Scenario 2 system boundaries.

For comparing the different systems of secondary Al smelting, a cradle-to-gate approach is considered, assessing the partial product life cycle of secondary Al ingots from the extraction of raw materials (i.e., fossil fuels and Al scraps) up to the production of the ingots. In that sense, upstream activities are included, considering the operation and manufacture of the technologies.

3.4 Life Cycle Inventory and Data Collection

The LCI consists of all the inputs and outputs data in terms of material, energy, emissions etc., for every process involved in the total impact evaluation of the plant.

For scenario 1, the LCI data was provided by the GaBi (the largest internally consistent LCI databases on the market today) drawn from the literature. the NG combustion is considered to

take place in industrial equipment. The smelter is simulated as a reverberatory furnace, operating between 700-800 °C, and followed by a casting process for the production of the final ingot product. The Al recovery and transport process is selected, accounting for the atmospheric, waterborne, and solid waste emissions representing process emissions only.

For scenario 2, the LCI data was mainly drawn from the literature. H₂ production by electrolysis process is provided by the GaBi database (marked with ‘ts’). A 64 kWe SOFC is selected for the production of high-grade heat and electricity. The cells will achieve high power densities allowing more than 80 % fuel utilization and can be operated from 700 °C to 800 °C. The SOFC operation has an electrical efficiency of at least 60 %, while the CHP efficiency is higher than 90 %. For the H₂ combustion, a 600 kW fired burner is used, designed to achieve complete combustion, while achieving optimal peak flame temperature for minimum NO_x formation, optimal combustion rate, optimal flame shape and pattern, and optimal radiant heat flux rates for optimal radiant heat transfer. A 45 kVA H₂ ICE is selected for delivering the medium grade-heat to the smelter and the required electricity to the SOFC, with a CHP efficiency of 70 %. The Al casthouse plant is equipped, followed by a casting process for the production of the final ingot product. The Al recovery and transport process is considered identical with scenario 1.

Table 1. LCI data for 1 FU production [44-46].

Flow	Amount for 1 FU production	Unit
H ₂ production/distribution to SOFC	12.6	kg
H ₂ production/distribution to Genset	0.868	kg
H ₂ production/distribution to Burner	37.1	kg
Total H ₂ consumption	50.5	kg
Al recovery/transport to Smelter	1 050	kg
ICE Genset to SOFC	35.7	MJ
SOFC to Smelter	786	MJ
Net electricity consumption	786	MJ
ICE Genset to Smelter	47.6	MJ
SOFC to Smelter	499	MJ
Burner to Smelter	4 450	MJ
Total Thermal energy consumption	4 996.4	MJ

3.5 Modelling in GaBi

In scenario 1, for the production of 1 tonne of secondary Al ingot, 216 m³ of NG were fed to the burner for combustion. The NG was transferred from the processing plant via trucks and trains, covering 42 900 kg·km and 2 560 kg·km respectively. Photovoltaics covered the 786 MJ electricity demand of the smelter. Lastly, the Al recovery and transport to the smelter process supplied 1050 kg of Al scrap, considering a material loss of almost 5 % in the smelting process. In scenario 2, for the production of 1 tonne of secondary Al ingot, 50.5 kg of H₂ were distributed among the SOFC, ICE and burner, 12.6 kg, 0.868 kg and 37.1 kg respectively. The three technologies supplied the total thermal energy demand of approximately 5000 MJ, by 499 MJ, 47.6 MJ and 4 450 MJ respectively. The SOFC was supplied 35.7 MJ of electricity from the ICE for its operation. As in scenario 1, the smelter was supplied with 786 MJ, in this case by the SOFC, and 1050 kg of Al scrap by the same Al recovery and transportation process, considering identical energy demand and material losses for identical smelters.

3.6 Life Cycle Impact Assessment

For this LCA study, midpoint categories have been applied to perform LCIA. The choice of impact categories was based on the recommendations of the FC Hy-Guidance as well as the scope of the study [47]. These impact categories are shown in Table 2.

Table 2. Life cycle impact categories.

Impact Category	Recommended Indicator	Selected Indicator	Unit
Climate Change	Global Warming Potential	Global Warming Potential (GWP) (CML 2001)	kg CO ₂ eq
Acidification	Accumulated exceedance method [48]	Acidification Potential (AP) (CML 2001)	kg SO ₂ eq
Eutrophication	Accumulated exceedance method	Eutrophication Potential (EP) (CML 2001)	kg Phosphate eq
Photochemical Ozone Formation	LOTOS-EUROS model consists of a detailed fate and exposure model for human health impacts [49]	Photochemical Oxidant Formation (POF) (ReCiPe)	kg NMVOC eq

4. Results and Discussion

Figure 4 depicts the LCIA results, showing the total value of the impact categories for the scenarios. It is evident, that deploying H₂ technologies can contribute to a reduction of more than 49 %, 81 % and 61 % of Global Warming Potential (GWP), Acidification Potential (AP) and Photochemical Oxidant Formation (POF) respectively while the Eutrophication Potential (EP) remains the same.

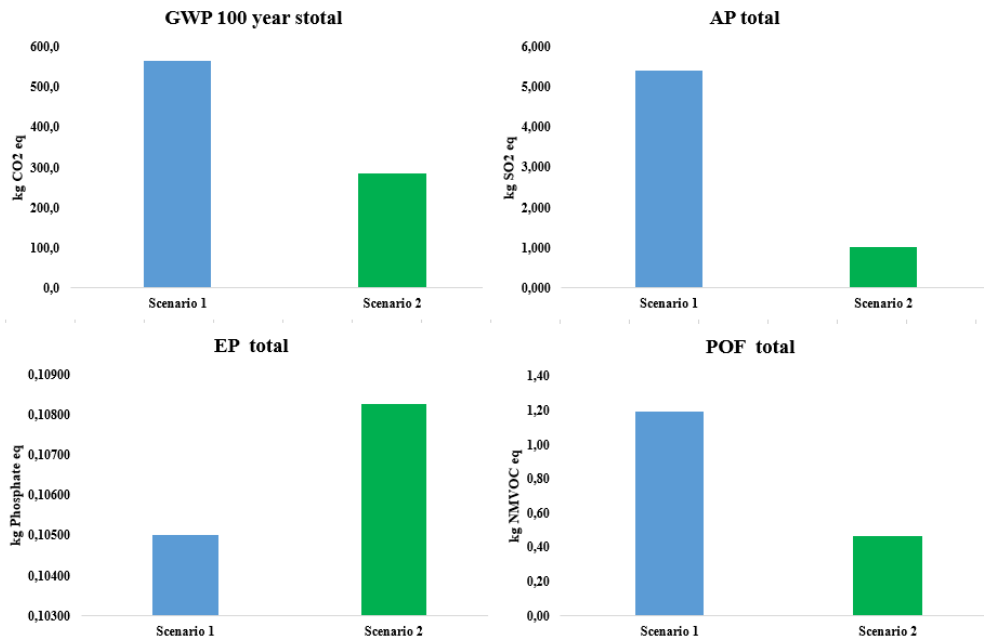


Figure 4. LCIA results for scenario 1 (NG) and scenario 2 (H₂).

GWP, AP and POF show a great reduction, due to the substitution of NG with H₂, thus enabling combustion in the absence of carbon and therefore limiting the CO₂ and CO emissions to almost zero. Specifically, in scenario 2, 100 % of the 84.7 kg CO₂ eq derives from the H₂ production and distribution, the Al scrap recovery and transport process and the manufacturing of the SOFC, ICE and burner, as shown in Figure 5. Therefore, the utilization of H₂ reduces the more than 560 kg CO₂ eq of scenario 1 to less than 285 kg CO₂ eq. In terms of AP, combustion of H₂ in the ICE and H₂ burner account for a reduction of more than 99 % in kg SO₂ eq, in comparison with scenario 1 (Figure 6). In terms of power supply, electricity from photovoltaics accounted for 7.83 kg CO₂ eq for the production of 1 tonne of secondary Al ingot, while H₂ power production systems accounted only for their manufacturing emissions (Figure 5). EP is the indicator showing the least reduction, due to the NO_x formation that is present in H₂ combustion (Figure 7). Despite that, H₂ combustion is still favourable in terms of NO_x, while the implementation of zero NO_x SOFC H₂ systems can minimize the need of H₂ combustion. It is also worth noting that utilising O₂-enriched combustion can further reduce the NO_x emissions of H₂ combustion. In terms of POF, the replacement of the NG processing, supplying and burning system with H₂ production and distribution systems and CHP technologies shows a reduction in kg of non-methane volatile organic compounds (NMVOK) eq of more than 84 % (Figure 8).

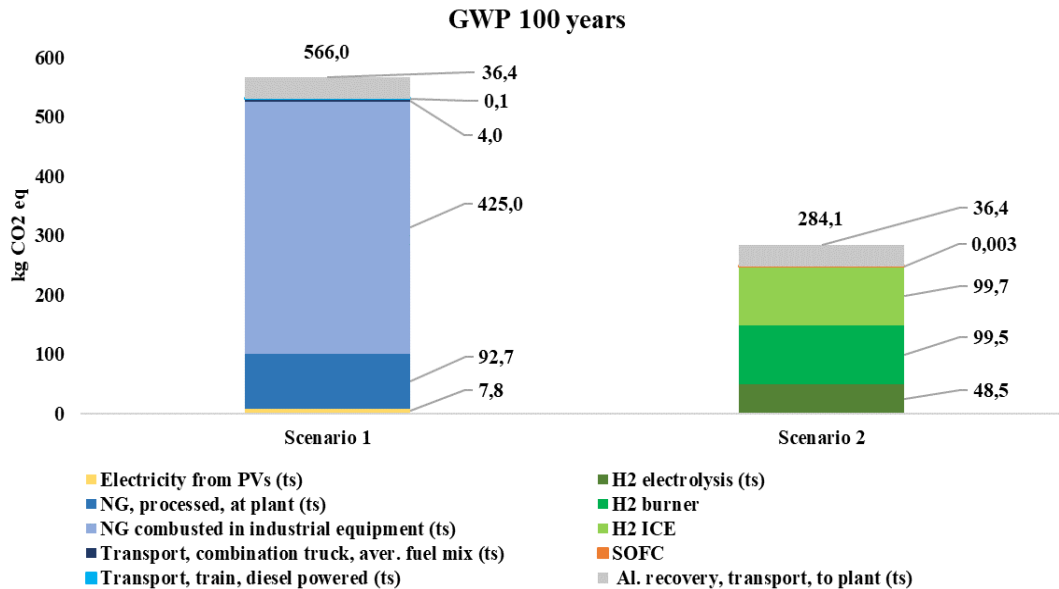
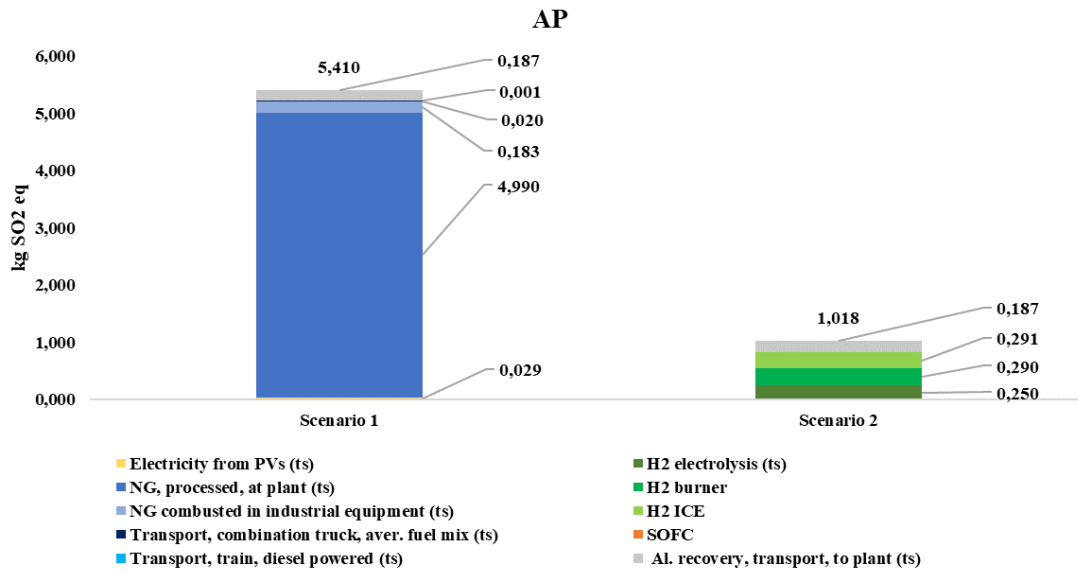
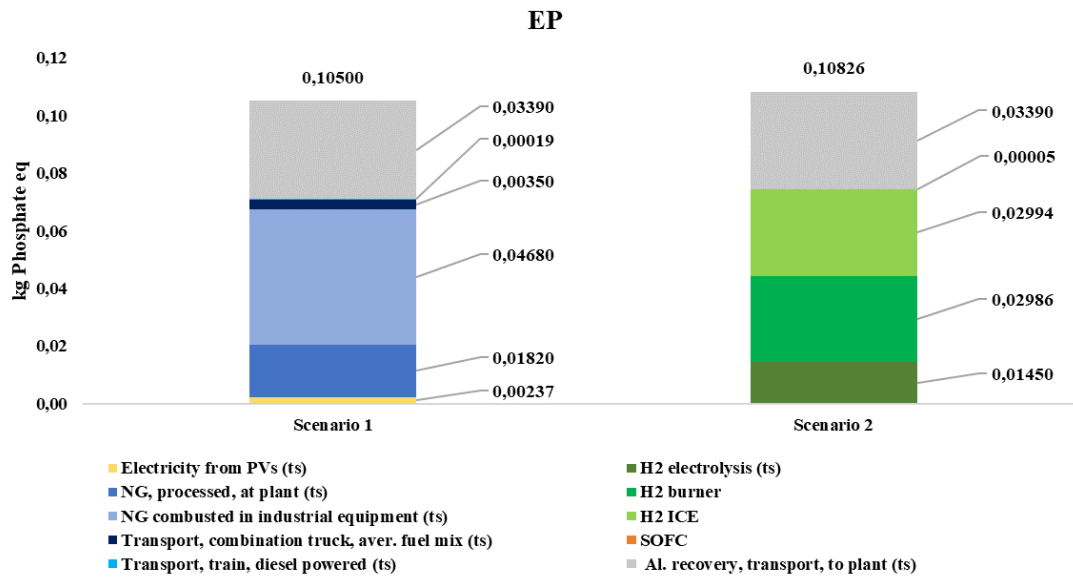


Figure 5. Life Cycle Impact Assessment for Scenario 1 & 2: Global Warming Potential (kg CO₂-eq.).



**Figure 6. Life Cycle Impact Assessment for Scenario 1 & 2:
Acidification Potential (kg SO₂-eq.).**



**Figure 7. Life Cycle Impact Assessment for Scenario 1 & 2:
Eutrophication Potential (kg phosphate-eq.).**

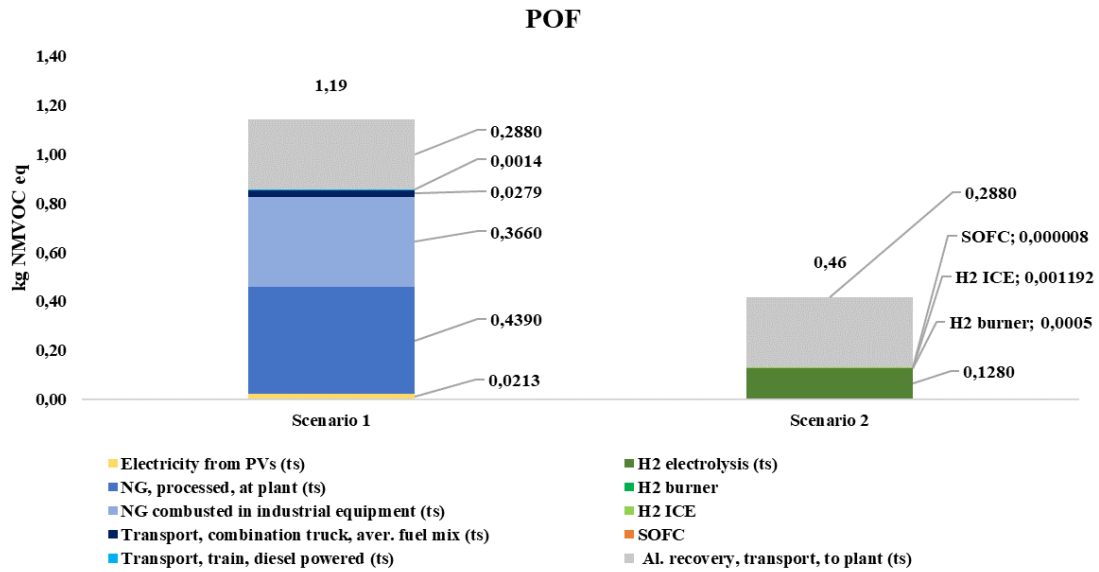
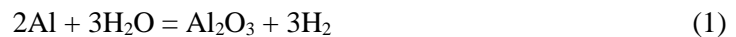


Figure 8. Life Cycle Impact Assessment for Scenario 1 & 2: Photochemical Ozone Formation (kg NMVOC-eq.).

As it is shown, the exploitation of H₂ technologies in a secondary Al smelting plant provides great potential for reducing the environmental impact of the involved processes. However, to ensure the green nature of the H₂-based CHP technologies (e.g., SOFC, H₂ ICE, etc.) in comparison to the conventional CHP production (NG burner), it is crucial to import to the plant clean H₂ (green or at least blue). It is mentioned also that H₂ production is classified in three main colour categories including the 'grey H₂' produced as a by-product of an industrial process, the 'blue H₂' produced through a production process where CO₂ is also produced then subsequently captured via Carbon capture and storage (CCS), and finally the 'green H₂' which is produced entirely from renewable sources.

An alternative to importing green H₂ to the plant would be the in-house H₂ generation by using recycled Al [50]. Such approaches have already found practical applications, with new plants enabling the generation of approximately 5 kg/h H₂ [51]. The main approach is by the reaction of Al with water streams [52]. The reaction for the H₂ production is as follows:



The molten Al is stationed in the vessel where water is introduced through inlet nozzles, resulting to the reaction and production of H₂ gas and heat to be withdrawn from the vessel. Subsequently, the withdrawn heat can be exploited within the production cycle. Therefore, the incorporation of H₂ production processes in the proposed scheme could further improve the environmental impact of the whole secondary Al production cycle.

5. Conclusions

Green H₂ offers a decarbonisation solution for EIIs, being an important enabler to meet the 2050 climate neutrality goals. The utilisation of H₂ into new production routes and the direct use for medium-high grade heating and electrification will be fundamental to decarbonise EU industry across a number of sectors. In EIIs, H₂ can be used for thermal energy delivery instead of fossil fuels, when combusted in furnaces, burners, ICE or boilers. However, it is crucial to consider the design and operative conditions of H₂ combustion in order to minimise the NO_x formation, associated to conventional H₂ burners, such as lower flame temperature, slower combustion, etc.

In this study, the methodology of LCA is applied in order to evaluate the environmental impact associated with the energy and material flows within a secondary Al smelting plant and validate the green nature of the H₂-based CHP technologies in comparison to the conventional CHP production. The results show the transition towards H₂ technologies to be highly beneficial in terms of both efficiency and emissions reduction. Incorporating ICE and SOFC systems for H₂-based high grade heat production substantially decreased the energy demand from outside sources. Additionally, the proposed scheme appeared to have almost 49 % less impact than the current practises in terms of GWP, 81 % in terms of AP and 61 % in terms of POF.

This proposed scheme can serve as a basis for further investigation on secondary self-sustained H₂-fuelled systems, supporting the main metallurgical processes. Further studies are recommended to address factors including the detailed techno-economic analysis of energy systems with integrated green H₂ production, which can provide to the EIs an additional role as decentralised green power stations.

6. References

1. *Transforming Extractive Industries for Sustainable Development*, 2021 [accessed on 1 July 2022], Available from: https://www.un.org/sites/un2.un.org/files/sg_policy_brief_extractives.pdf.
2. *Internal Market, Industry, Entrepreneurship and SMEs* [accessed on 1 July 2022], Available from: https://ec.europa.eu/growth/industry/strategy/energy-intensive-industries_en.
3. *Material efficiency in clean energy transitions*, 2019 [accessed on 1 July 2022], Available from: <https://www.iea.org/reports/material-efficiency-in-clean-energy-transitions>.
4. *Fourth Quarter and Full Year 2020 Trading Update*, 2020 [accessed on 1 July 2022], Available from: <https://www1.hkexnews.hk/listedco/listconews/sehk/2021/0208/2021020800023.pdf>.
5. *The Energy Transition and Extractive Industries Development in the Asia-Pacific Region I* [accessed on 1 July 2022], Available from: https://www.unescap.org/sites/default/d8files/event-documents/ANNEX%20IV-%20BACKGROUND%20PAPER_0.pdf.
6. Resource extraction responsible for half world's carbon emissions, 2019 [accessed on 1 July 2022], Available from: <https://www.theguardian.com/environment/2019/mar/12/resource-extraction-carbon-emissions-biodiversity-loss>.
7. *Metals & mining decarbonisation and sector disclosure*, 2021 [accessed on 1 July 2022]; Available from: <https://think.ing.com/articles/metals-mining-decarbonisation-sector-disclosure>.
8. European Aluminium, *Digital Activity Report 2020-2021*, in *Market Overview*. 2021.
9. Simon Öberg et al., Exploring the competitiveness of hydrogen-fueled gas turbines in future energy systems, *International Journal of Hydrogen Energy*, 2022, **47**(1): p. 624-644 DOI: <https://doi.org/10.1016/j.ijhydene.2021.10.035>.
10. *Eurometaux - European Association of Metals, Closures and curtailments in Europe's non-ferrous metals industry because of high electricity prices, A call for concrete actions to address the critical situation*, P.o.t.E.C.U.v.d. Leyen;, P.o.t.E.C.C. Michel;, and A.P.o.t.E.P.R. Metsola, Editors, 2022.
11. Secondary Production 101, [accessed on 15 July 2022]; Available from: <https://www.aluminum.org/secondary-production-101>.
12. Wenjing Wei, Energy Consumption and Carbon Footprint of Secondary Aluminum Cast House [accessed on 15 July 2022]; Available from: <https://www.diva-portal.org/smash/get/diva2:620633/FULLTEXT01.pdf>.

13. *Hydrogen scaling up, a sustainable pathway for the global energy transition*, 2017 [accessed on 1 July 2022]; Available from: <https://hydrogencouncil.com/wp-content/uploads/2017/11/Hydrogen-scaling-up-Hydrogen-Council.pdf>.
14. Stefan Luidold and Helmut Antrekowitsch, Hydrogen as a reducing agent: State-of-the-art science and technology, *JOM*, 2007, **59**(6): p. 20-26 DOI: 10.1007/s11837-007-0072-x.
15. Daniel Spreitzer and Johannes Schenk, Reduction of Iron Oxides with Hydrogen—A Review, *steel research international*, 2019, **90**(10): p. 1900108 DOI: <https://doi.org/10.1002/srin.201900108>.
16. Fuels - Higher and Lower Calorific Values [accessed on 15 July 2022]; Available from: https://www.engineeringtoolbox.com/fuels-higher-calorific-values-d_169.html.
17. Bob Langstine John Guarco, Michael Turner, Hydrogen – The Alternative Fuel, 2021 [accessed on 1 July 2022]; Available from: https://info.zeeco.com/hubfs/Articles/Hydrogen-The-Alternative-Fuel_ABMA-Spring-2021_Zeeco-Article_H2-Firing-vs-Natural%20Gas%20Combustion.pdf?hsLang=en.
18. Hydrogen co-combustion in ICE, 2019 [accessed on 14 July 2022]; Available from: https://theicct.org/sites/default/files/2_Campe_H2_combustion_ICE_PUBLIC.pdf.
19. *Why SOFC Technology?* [accessed on 1 July 2022]; Available from: <https://www.energy.gov/fecm/why-sofc-technology>.
20. Solid Oxide Fuel Cells, Opportunities for a clean energy future, 2019 [accessed on 1 July 2022]; Available from: <https://elcogen.com/wp-content/uploads/2019/04/elcogen-sofc-white-paper-2019.pdf>.
21. Yoshinori Kobayashi et. al., Development of Next-Generation Large-Scale SOFC toward Realization of a Hydrogen Society, 2015 [accessed on 1 July 2022]; Available from: https://power.mhi.com/jp/randd/technical-review/pdf/index_01e.pdf.
22. MHPS Sought First Order For Hybrid Power Generation System [accessed on 1 July 2022]; Available from: <https://www.powerworldanalysis.com/mhps-sought-first-order-hybrid-power-generation-system/>.
23. Jörg Leicher et al., The Impact of Hydrogen Admixture into Natural Gas on Residential and Commercial Gas Appliances, *Energies*, 2022, **15**(3): p. 777.
24. Michela Costa et al., Hydrogen Addition to Natural Gas in Cogeneration Engines: Optimization of Performances Through Numerical Modeling, *Frontiers in Mechanical Engineering*, 2021, **7** DOI: 10.3389/fmech.2021.680193.
25. Fuwu Yan et al., Application of hydrogen enriched natural gas in spark ignition IC engines: from fundamental fuel properties to engine performances and emissions, *Renewable and Sustainable Energy Reviews*, 2018, **82**, 1457-1488 DOI: <https://doi.org/10.1016/j.rser.2017.05.227>.
26. Yasin Karagöz et al., Effect of hydrogen–diesel dual-fuel usage on performance, emissions and diesel combustion in diesel engines, *Advances in Mechanical Engineering*, 2016, **8**(8): p. 1687814016664458 DOI: 10.1177/1687814016664458.
27. Mike Menzies, Hydrogen: The Burning Question, 2019 [accessed on 1 July 2022]; Available from: <https://www.thechemicalengineer.com/features/hydrogen-the-burning-question/>.
28. Sebastian Verhelst and Thomas Wallner, Hydrogen-fueled internal combustion engines, *Progress in Energy and Combustion Science*, 2009, **35**(6): p. 490-527 DOI: <https://doi.org/10.1016/j.pecs.2009.08.001>.
29. Ho Lung Yip et al., A Review of Hydrogen Direct Injection for Internal Combustion Engines: Towards Carbon-Free Combustion, *Applied Sciences*, 2019, **9**: p. 4842 DOI: 10.3390/app9224842.
30. Hayder A. Alrazen and K. A. Ahmad, HCNG fueled spark-ignition (SI) engine with its effects on performance and emissions, *Renewable and Sustainable Energy Reviews*, 2018, **82**, 324-342 DOI: <https://doi.org/10.1016/j.rser.2017.09.035>.
31. P Visciglio, CFD analysis of combustion in CNG/HCNG engines, 2019.

32. Ankur Mittal et al., Oxygen Enrichment Technology—An Innovation for Improved Solid Fuel Combustion and Sustainable Environment, in *Enhancing Future Skills and Entrepreneurship*, 2020, Cham: Springer International Publishing.
33. Jun Li et al., Combustion and Heat Release Characteristics of Biogas under Hydrogen- and Oxygen-Enriched Condition, *Energies*, 2017, **10**(8) DOI: 10.3390/en10081200.
34. Adamantia Lazou et al., On the Direct Reduction Phenomena of Bauxite Ore Using H₂ Gas in a Fixed Bed Reactor, *Journal of Sustainable Metallurgy*, 2020, **6**(2), 227-238 DOI: 10.1007/s40831-020-00268-5.
35. M. Samouhos et al., Controlled reduction of red mud by H₂ followed by magnetic separation, *Minerals Engineering*, 2017, **105**, 36-43 DOI: <https://doi.org/10.1016/j.mineng.2017.01.004>.
36. Masoud Moshtaghi et al., Hydrogen absorption rate and hydrogen diffusion in a ferritic steel coated with a micro- or nanostructured ZnNi coating, *Electrochemistry Communications*, 2022, **134**, p. 107169 DOI: 10.1016/j.elecom.2021.107169.
37. Ivan Bunaziv et al., Metallurgical Aspects in the Welding of Clad Pipelines—A Global Outlook, *Applied Sciences*, 2019, **9**(15) DOI: 10.3390/app9153118.
38. Matthew S. Brown and Craig B. Arnold, Fundamentals of Laser-Material Interaction and Application to Multiscale Surface Modification, in *Laser Precision Microfabrication*, K. Sugioka, M. Meunier, and A. Piqué, Editors, 2010, Springer Berlin Heidelberg: Berlin, Heidelberg, 91-120.
39. Ondřej Nenadl et al., The Prediction of Coating Geometry from Main Processing Parameters in Laser Cladding, *Physics Procedia*, 2014, **56**, 220-227 DOI: <https://doi.org/10.1016/j.phpro.2014.08.166>.
40. ISO 14040:2006 - Environmental management — Life cycle assessment — Principles and framework, 2006 [accessed on 12 July 2022]; Available from: <https://www.iso.org/standard/37456.html>.
41. ISO 14044:2006 - Environmental management — Life cycle assessment — Requirements and guidelines, 2006 [accessed on 12 July 2022]; Available from: <https://www.iso.org/standard/38498.html>.
42. European Platform on Life Cycle Assessment [accessed on 12 July 2022]; Available from: <https://eplca.jrc.ec.europa.eu/>.
43. Life Cycle Assessment [accessed on 12 July 2022]; Available from: <https://gabi.sphera.com/international/index/>.
44. Carlo Strazza et al., Life Cycle Assessment and Life Cycle Costing of a SOFC system for distributed power generation, *Energy Conversion and Management*, 2015, **100**, 64-77 DOI: <https://doi.org/10.1016/j.enconman.2015.04.068>.
45. B. Fumey et al., Ultra-low NO_x emissions from catalytic hydrogen combustion, *Applied Energy*, 2018, **213**: p. 334-342 DOI: <https://doi.org/10.1016/j.apenergy.2018.01.042>.
46. Daniele Candelaresi et al., Comparative life cycle assessment of hydrogen-fuelled passenger cars, *International Journal of Hydrogen Energy*, 2021, **46**(72), 35961-35973 DOI: <https://doi.org/10.1016/j.ijhydene.2021.01.034>.
47. A. Zamagni P. Masoni, Guidance Document for performing LCAs on Fuel Cells and H₂ Technologies, 2011 [accessed on 12 July 2022]; Available from: <http://hytechcycling.eu/wp-content/uploads/HY-Guidance-Document.pdf>.
48. Jyri Seppälä et al., Country-dependent Characterisation Factors for Acidification and Terrestrial Eutrophication Based on Accumulated Exceedance as an Impact Category Indicator (14 pp), *The International Journal of Life Cycle Assessment*, 2006, **11**(6), 403-416 DOI: 10.1065/lca2005.06.215.
49. Rosalie van Zelm et al., European characterization factors for human health damage of PM₁₀ and ozone in life cycle impact assessment, *Atmospheric Environment*, 2008, **42**(3), 441-453 DOI: <https://doi.org/10.1016/j.atmosenv.2007.09.072>.

50. Esam Elsarrag et al., The production of hydrogen as an alternative energy carrier from aluminium waste, *Energy, Sustainability and Society*, 2017, **7**(1), p. 9 DOI: 10.1186/s13705-017-0110-7.
51. *A New Verification Plant Designed to Generate Power Using Hydrogen Extracted from Aluminum-Based Waste Completed*, 2016 [accessed on 1 July 2022]; Available from: https://www.nedo.go.jp/english/news/AA5en_100204.html.
52. Nancy W. Stauffer, Using aluminum and water to make clean hydrogen fuel—when and where it's needed, 2021 [accessed on 1 July 2022]; Available from: <https://energy.mit.edu/news/using-aluminum-and-water-to-make-clean-hydrogen-fuel-when-and-where-its-needed/>.