UNIVERSITY OF
CAMBRIDGE

H2Upgrade

Distributed and flexible H_2 production from waste streams

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Contents

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Glossary

ATEX - explosive regulations, **BP** - British Petroleum, **CAPEX** - capital expenditure, **CEB** -Department of Chemical Engineering and Biotechnology, **CLC** - chemical looping combustion, **CO** - carbon monoxide, **CUED** - Department of Engineering, **EU** - European Union, **GHG** - greenhouse gas, **GR2L** - Gas Recovery and Recycle Ltd, **H_2** – hydrogen, **HVO** - Hydrotreated vegetable oil, **LCA** - life cycle analysis, **MO_x, MO_{x-1}** - metal oxide materials, **$MtCO_2$** - megatonne CO_2, **O** - oxygen, **Owlstone** - vapour delivery system, **PBR** - Packed-bed reactor, **REG Synthetic fuel** – HVO producer, **TGA** - Thermogravimetric analyser, **UK –** the United Kingdom, **US -** the United States, **wt** – weight

1. Executive summary

The project focused on a feasibility study of new technology for producing H_2 from waste streams, such as organic solvents and gases. The goal of the project was to demonstrate the process and analyse the pathway to commercialising such a technology.

The project consortium is led by the University of Cambridge and includes two Departments: Chemical Engineering and Biotechnology (CEB) and Engineering (CUED). The project was performed in partnership with Gas Recovery and Recycle (GR2L) Ltd.

This report summarises the H2Upgrade technology and its potential, assessed in the project. H2Upgrade uses a chemical looping approach for converting combustible components into hydrogen and CO_2 using metal oxides. The ambition of this technology is to produce hydrogen from under-valued waste streams, *e.g.* spent solvents, mixtures of solvents, and gases, that are currently sent to incineration or flared. Potential low-value waste streams are discussed, and their applicability for H_2 production *via* H2Upgrade is assessed. Then, materials made of metal oxides (MO_x), which are an integral part of the technology, are described, summarising the analysed materials that react with selected waste streams. Results from two experimental rigs are discussed, demonstrating H_2 production *via* H2Upgrade. Finally, the consequences of implementing H2Upgrade are discussed, including the environmental impact and saved greenhouse gas emissions. The report ends with a short description of the possible rollout potential and route to market.

2. Introduction

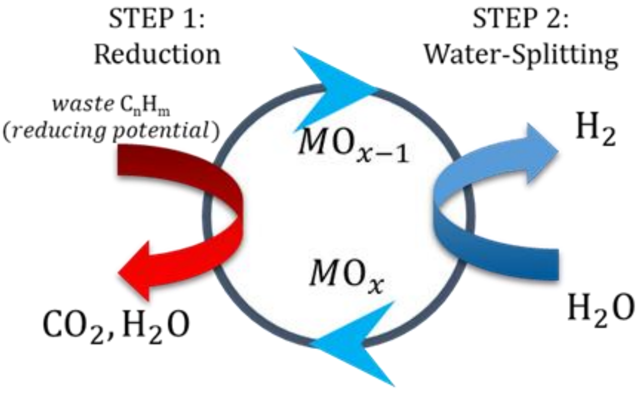
2.1. Overview of the project

H2Upgrade technology for H_2 generation is based on thermochemical water splitting and utilisation of waste streams. The goal of the Phase 1 project is to demonstrate H_2 production *via* H2Upgrade using identified, attractive, low-value waste streams.

The technology is based on reactions with solid materials, such as ferrites and manganates, with no requirement for precious metals. When heated to high temperatures and pre-treated with reducing components from the waste streams (step 1), the materials gain the ability to efficiently split water in a thermochemical way, producing high-purity H_2 (step 2), see Fig. 1.

The 2-step, a cyclic process, is relatively well-known, taking from the chemical looping approach, but has not been fully exploited. The usually-proposed processes for H_2 production using chemical looping are commonly based on CH_4 reforming rather than water splitting, but the main point of using solid materials to deliver oxygen to reactions remains unchanged[1]. The benefit of using H_2O as a source of H_2 is the possibility of avoiding CH_4 – instead, using other hydrocarbons, such as low-value waste streams. Thus, in the H2Upgrade project, we deliberately avoided natural gas and identified potential waste streams instead.

Depending on their availability, the technology can be used with waste streams of different properties, leading to a new, versatile and flexible pathway to H_2 production. For example, applying the waste streams from landfills, steel-making, or utilising hydrocarbons from solvent disposal.



$$\text{STEP1: } C_nH_m + yMO_x \rightarrow nCO_2 + m/2H_2O + yMO_{x-1}$$

$$\text{STEP2: } MO_{x-1} + H_2O \rightarrow MO_x + H_2$$

Figure 1 Thermochemical water-splitting using metal oxides, MO_x. After reacting with waste streams (step 1), the reduced metals oxide, MO_{x-1} is ready to split water (step 2).

2.2. Objectives

The project focused on demonstrating the H2Upgrade processes with waste streams and water, looking for suitable MOx materials, and trying to shift the operating window for reactions in Fig. 1 to a low-temperature range. The main project objectives (O1-4) have been defined as follows:

O1) Identify **suitable wastes** and **MO_x materials** for H2Upgrade, minimising the operating temperature in both steps of the process

O2) Demonstrate **H2Uprgade with different waste streams** in experiments from mg to 10 g of MO_x.

O3) Assess and minimise H2Upgrade **environmental impact.**

O4) First-pass design of a small-scale H2Upgrade unit.

Those objectives were approached in four work packages, 9 project deliverables, and 4 reporting deliverables.

3. Results and conclusions

3.1. Assessment of waste-streams

The Waste Data Interrogator for England waste management sites published annually by the Environment Agency has been used to quantify wastes[2–4], which can work as reducing waste streams in H2Upgrade. A dedicated class for "Spent solvents" is selectable under the Substance-Oriented Classification (SOC) Sub-Category. Filtering "Spent solvents" with Incineration fate shows that up to 26,000 tonnes of this type of waste stream were received by England's waste management sites in 2020 and incinerated. The Waste Data Interrogator for England provides a sense of scale for the amount of the wastes circulated in the country as the waste data "Origin Region" column also includes Wales, Scotland and Northern Ireland.

The actual amount of reducing waste streams potentially available for H_2 production will differ because various streams contain various impurities, and their role has not yet been assessed in the H2Upgrade process. Also, compositions of the waste mixtures are not as easily deducible since the producers do not disclose detailed information to maintain commercial confidence. Nevertheless, after analysing the "Spent solvents" waste category, the following organic compounds were identified as attractive reducing waste streams:

- Acetone (C_3H_6O), solvents, paint, varnishes, lacquers, plastics, fibres, lipids, rubber etc.
- Ethanol (C_2H_5OH), solvents, lipids, resins, waxes etc.
- Butanol (C_4H_9OH), solvents, coatings, varnishes, resins, gums, dyes, camphor, vegetable oils, dyes, fats, waxes, resins, shellac, rubbers, alkaloids etc.
- Toluene (C_7H_8), solvents, paints and coatings, gums, resins, rubber, glues etc.
- Glycerol ($C_3H_8O_3$), Dissolves food flavourings and colourings, personal care products (i.e. toothpaste) etc.
- Heptane (C_7H_{16}), Gasoline ingredient, dissolves inks, paints, coatings, plastic, adhesives, sealants, etc.
- Gas mixtures with H_2, CO, NH_3, and waste gases from industrial processes.
- Mixtures of waste streams containing one of the listed components as the main component.

Whether a waste stream reacts with a solid material in step 1 of the process (Fig.1) depends on the "reducing potential" of that waste stream, that can be assessed through theoretical calculations using thermodynamic data. Taking iron oxide (Fe_2O_3) as an exemplary MOx, three possible sub-steps in reduction that, in reverse, can split water can be considered, namely: (1) Fe_3O_4 to $Fe_{0.947}O$ (Wustite), (2) $Fe_{0.947}O$ (Wustite) to Fe, (3)

Fe_3O_4 to Fe. The thermodynamic conditions for those three transformations are described with the equilibrium P_{O_2} from the reaction: $MO_{x-1} + \frac{1}{2}O_2 = MO_x$ or the equivalent P_{CO}/P_{CO_2}. Those values can be interpreted as the theoretical indicators of the "reducing potential". Here, P_{CO}/P_{CO_2} was assessed for waste streams containing "O", using MTDATA software, and looking at reactions with iron oxides, as presented in Fig. 2. For the waste streams that do not contain oxygen in their structure, *i.e.* toluene, H_2, heptane, the equilibrium P_{O_2} is infinitely low, translating to "infinite" reducing potential. However, for other streams, which contain O, the "reducing power" need to be assessed carefully.

Figure 2 demonstrates at which temperature the reaction is thermodynamically feasible, or in other words, at which temperature the "reducing power" of a waste stream becomes sufficient to trigger the reaction. For example, glycerol can only reduce the discussed oxides of iron above ~630ºC (903 K). Obtained results allow us to conclude the feasible operating temperature window for the H2Upgrade rectors. As can be seen from Fig. 2, one type of MOx material can operate with different waste streams, provided the reaction temperature is adjusted.

Although the results are discussed in reference to MOx of iron, the potential of "reducing power" for the considered waste streams remains independent of the type of MOx used. Thus, the next goal is to select suitable MOx, which can reduce when exposed to the "reducing power" available in the waste streams.

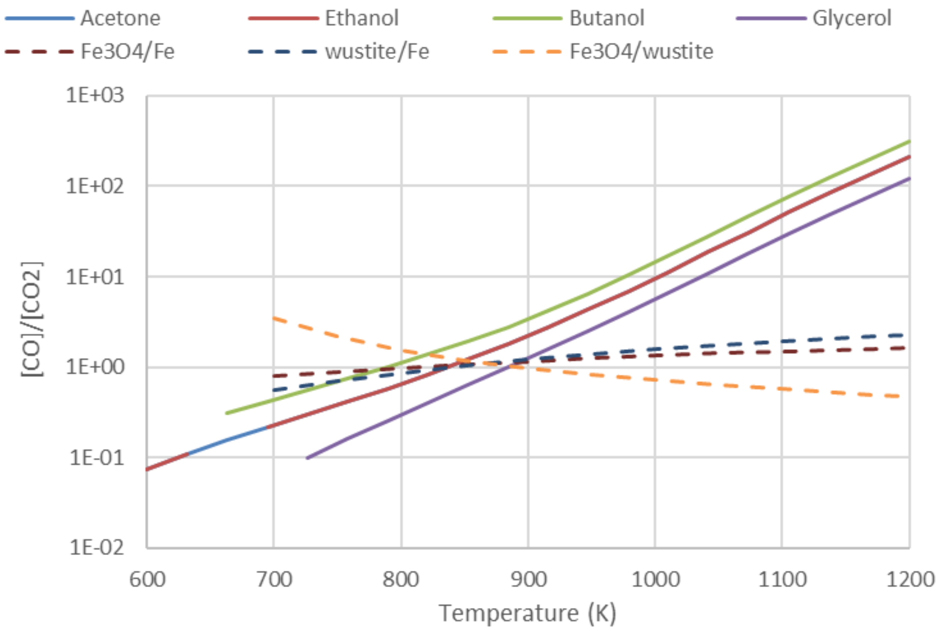


Figure 2 Equilibrium diagram showing the phase transition of iron oxides. Also shown are the “reducing powers” of the oxygenated solvents found from a simplified calculation.

3.2. Assessment of impurities in typical waste-streams

Waste streams from industry typically contain various impurities. Seyler *et al.* made a general assumption of waste solvents for incineration having a composition of 30wt% water and 70wt% organic solvents, irrespective of the type of solvent[5]. Acetone-water waste solutions commonly contain 0.15 – 0.35wt% of dichloromethane, with 60 – 70wt% acetone and 30 – 40 wt% water[6]. Dichloromethane also often accompanies waste streams from butanol recovery, with 50 – 90wt% n-butanol, 5 – 45wt% dichloromethane, and 5 – 20wt% water[7]. In the case of waste streams containing toluene, a case study considered a waste output composition[7] of 41.3wt% toluene, $35.3\%_{wt}$ water, $21.3\%_{wt}$ of dimethoxyethane (often used in the production of lithium-ion batteries), 1.3wt% 1-ethoxy-1-methoxy ethane (food additive), and remainder 0.7wt% of other undefined impurities. Waste gas streams containing heptane have been modelled with 36 – 50wt% heptane, 37 – 50 wt% diisopropyl ether (also an industrial solvent), and 0 – 27wt% diethyl ether[8]. Waste glycerol from biodiesel production commonly consists of 70wt% glycerol, ~10 wt% water, and salt[9]. All things considered, spent solvents could be simulated in laboratory settings with 40 – 70wt% solvent, 0 – 30wt% water, 0 – 40wt% other solvents and/or representative substances from their industrial applications, with a possible input of 0 – 20wt% salt.

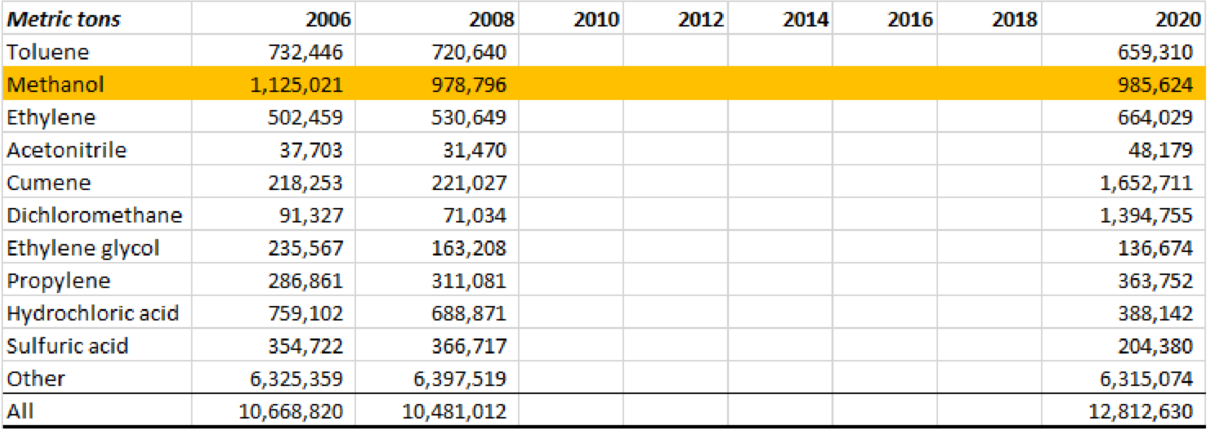
Aside from the possible pre-processing being filtration for removing suspended solids, different impurities will pose different challenges during operation. The presence of water could lead to phase separation and problems with feeding. The presence of other solvents and organic compounds could impact Step 1 of H2Upgrade reduction – either lowering or raising the temperature requirements. Other substances, like salt and/or TiO_2, may cause the deactivation of MOx materials, reducing their cyclability.

Similarly, the influence of organic impurities has been shown to be negligible when performing experiments with denatured ethanol containing isopropyl alcohol or methanol - common denaturants. Further investigations of impurities specific to potential waste streams would be needed before the implementation of H2Upgrade to coexist with various industrial processes.

3.3. Other opportunities

After analysing the waste streams information in the UK and US prepared by Elucidare, we extended the list, adding methanol and propylene. According to the EPA, waste methanol production reached over 985,000 tonnes in 2020. Of this amount, over 240,000 tonnes were incinerated or stored and, thus, potentially available for H2Upgrade. For propylene, the production of this waste stream reached over 388,000 tonnes, most of which were flared with no heat recovery or used for incineration. Thus, this stream is attractive, as it can be transformed into a high-quality stream of high-purity H_2.

Table 1. Waste production rates (tonnes/year) in the US, disclosed by the Environmental Protection Agency. Source: Elucidare Ltd.



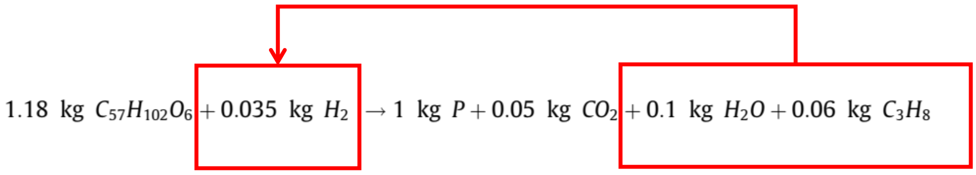
Metric tons	2006	2008	2010	2012	2014	2016	2018	2020
Toluene	732,446	720,640						659,310
Methanol	1,125,021	978,796						985,624
Ethylene	502,459	530,649						664,029
Acetonitrile	37,703	31,470						48,179
Cumene	218,253	221,027						1,652,711
Dichloromethane	91,327	71,034						1,394,755
Ethylene glycol	235,567	163,208						136,674
Propylene	286,861	311,081						363,752
Hydrochloric acid	759,102	688,871						388,142
Sulfuric acid	354,722	366,717						204,380
Other	6,325,359	6,397,519						6,315,074
All	10,668,820	10,481,012						12,812,630

Working with toxic gaseous streams, such as CO, would be feasible in H2Upgrade, as the technology would already need to comply with safety regulations of working in dangerous and explosive atmospheres (gas group IIC, see D.3.3).

Hydrotreated vegetable oil

Hydrotreated vegetable oil (HVO) is a renewable diesel produced by adding H_2 to vegetable oil. The product has excellent properties with reduced emissions, and it can be used in all types of diesel engines as a blending component or in pure form.

As shown below, propane is generated as a by-product of the hydrotreatment of used cooking oil. Here, *P* represents the hydrogenated product (bio-diesel). Besides *P*, the process leads to the production of CO_2, H_2O and propane, and all three are treated as waste products.



$$1.18\ \text{kg}\ C_{57}H_{102}O_6 + 0.035\ \text{kg}\ H_2 \rightarrow 1\ \text{kg}\ P + 0.05\ \text{kg}\ CO_2 + 0.1\ \text{kg}\ H_2O + 0.06\ \text{kg}\ C_3H_8$$

Here, we envisage the synergistic application of the H2Upgrade process. H2Upgrade can support the HVO route by converting propane into hydrogen, which could then be used in the hydrotreatment step. Currently, the HVO process is used in commercial installations by Phillips 66, Neste, BP, Honeywell/Eni, Topsoe, H-Bio, Diamond Green Diesel, REG Synthetic Fuels.

HVO operators are under severe pressure to identify green hydrogen solutions. The demand for HVO is growing worldwide, as evidenced by BP's recent strategic investment into HVO to become the UK's largest provider of low-emission hydrogenated vegetable oil fuels. Industry heavyweight NESTE has secured EU funding to develop green hydrogen processing at its HVO facilities in Finland and the Netherlands.

The HVO process was originally not on our radar (milestone 1), but it offers an exciting opportunity for large-scale deployment of H2Upgrade (possibly, in parallel to the Phase 2 project). For now, in Phase 1 H2Upgrade, we contacted Philips 66, the operator of the UK's only HVO refinery in Humberside. We contacted Robinson Brothers, which provides catalytic hydrogenation services[10] to discuss the techno-economic case for H2Upgrade.

Whisky distilleries

During this assignment, we contacted Ethimex, the UK's largest pure alcohol distributor for the spirits industry, who pointed us towards the growing demand for hydrogen within the Scottish whisky industry. There, H_2 is proposed as a carbonless fuel.

The whisky industry is one of the main industries in Scotland and is one of the energy-intensive industries, where the heat demand for the production process alone typically requires 60 MJ or 17 kWh per litre of alcohol. This is complemented by a similar amount of energy for the other parts of the distilleries' operation.

Multinational whisky distillery Diageo aims to reach net zero by 2030. Reportedly, the company is preparing to utilise hydrogen at all production sites. In January 2021, 17 distilleries across the UK received the first phase of £10 million in government funding to go green; of those, 10 analysed the feasibility of switching their fuels to H_2. Also, 11 distilleries across Scotland, including Highland Park and the Orkney Distillery in Kirkwall, will commence green innovations thanks to the government backing, helping them harness energy sources such as low-carbon hydrogen to power their operations.

It occurs to us that H2Upgrade could be used to convert the Acetone-Butanol-Ethanol (ABE) generated by the fermentation process (see Fig. 3) into hydrogen. Preliminary

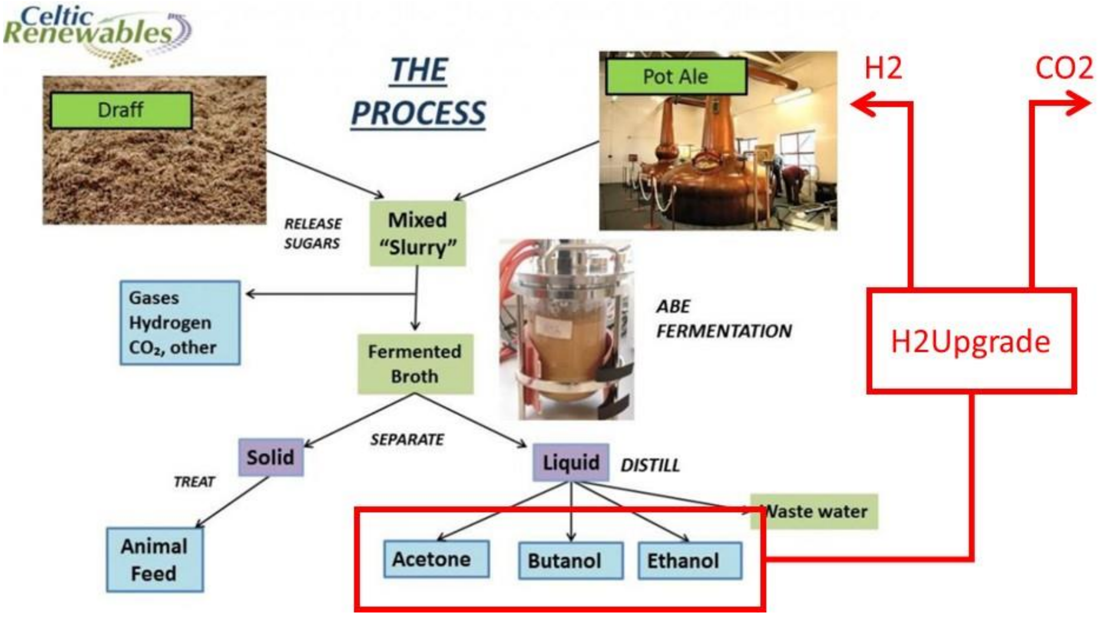


Figure 3 Hydrogen production for whisky distilleries via ABE fermentation and H2Upgrade. Source: Celtic Renewables graphic modified by Elucidare.

calculations suggest the H_2 generated by the H2Upgrade process would be sufficient to support 21% of the energy requirements of a modern malt whisky distillery such as InchDairnie and 11% for older distilleries (details in Table 2).

We contacted Celtic Renewables and Diageo to discuss the techno-economic case for H2Upgrade within the distillation waste industry.

Table 2: Hydrogen generation and energy recycling via *ABE and H2Upgrade*

	Unit	**Scotland: All malt distilleries**	**InchDairnie**
Distilleries	#	131	1
Pot ale per litre whisky	L/L	10	10
Whisky production	million L	400.9	2.9
Alcohol production	million L	254.6	1.8
Alcohol strength	%	63.50%	63.5%
Waste production	million L	4009.5	29.6
ABE yield	million L	31.0	0.2
Hydrogen production	million kg	8.0	0.060
HHV - H2	million kWh	268.6	1.986
Energy demand per kg alcohol	kWh/L	10.0	5.0
Energy demand	Million kWh	2546.0	9.4
%Energy from ABE	%	11%	21%

Source: Elucidare Limited

3.4. Contacting stakeholders

Here, we collaborated with an external consultant, Elucidare Ltd. First, we prepared an online form to map potential interest in H_2 production from waste. The form was sent out to 197 companies. This was followed up with further email correspondence and calls to 38 companies who expressed interest in H2Upgrade. Simultaneously, Dr Grant contacted companies from the GR2L client network.

Next, we held face-to-face or online meetings to discuss the ongoing Phase 1 project and the plans and ambitions for Phase 2. We continue discussing the technology with new companies.

3.5. Assessment of MOx materials

Besides Fe-oxides, other candidate MOx materials have been described for water-splitting processes. Those can be divided into stoichiometric and non-stoichiometric oxides. Stoichiometric metal oxides tend to have low cyclic stability and require relatively high reduction temperatures. Non-stoichiometric oxides, such as perovskites, can have the oxygen removed at lower temperatures but offer lower oxygen capacity.

The selection of MOx candidates requires considering a range of various factors, such as their reactivity, safety of operation, environmental impact and costs. Looking at the considered reactions, a suitable MOx should show fast redox kinetics in the considered temperature range, good oxygen capacity, and cycling stability. The multidimensionality of the material assessment makes the selection of MOx impossible in a single-pass exercise. Thus, a large list of materials is desirable to allow selection refinements.

For the assessment of materials in H2Upgrade, two approaches were implemented:

(1) analysis of the literature, screening for MOx used specifically for water splitting or CO_2 splitting. Here, CO_2 splitting to CO is included because the requirements of this reaction are similar to those for H_2O to H_2 (their Gibbs free energies are similar, e.g. 2.12 eV for H_2O and 2.23 eV for CO_2 at 500ºC).

(2) analysis of the theoretical candidate materials whose properties were predicted using computational modelling.

A list of 54 candidate materials was identified from the literature screening, looking at CO_2 or H_2O splitting rates, the temperature at which the material was characterised, the total yield of obtained CO or H_2, and the offset temperature of reactions. Some non-stoichiometric materials were ignored in the first instance because of the overlap with the results from the theoretical screening. Selected 9 candidate materials (based on Fe_2O_3, $LaFeO_3$, and $SrFeO_3$ with support structures) were synthesised in 2 to 5 g batches and used in experiments.

Screening of computationally identified materials was carried out on a materials list published by the Li Group[11] from the University of North Carolina, US. We discussed the project with Prof. Li during his visit to Cambridge in July. We focused on the 600k of materials, analysed for the energy of oxygen donation and uptake at 400ºC, treating them as a proxy for low-temperature reactions. The candidate materials were analysed by looking at the energy of reduction/oxidation and metallic components. Some materials were eliminated because of the toxicity, stability, or cost issues, ultimately reducing the set of candidate MOx to ~600 materials. Of those, some overlapped with screening results from the literature.

A further selection of candidate materials was based on the simplicity of material preparation and potential environmental problems. In total, 15 samples of various MOx were prepared for experiments.

3.6. Interaction of MOx materials with waste streams in H2Upgrade reactions

3.6.1. Thermogravimetric experiments (TGA)

TGA experiments provide information on the mass changes that a sample of MOx undergoes when exposed to a steady gas flow of the desired composition under a controlled heating and/or cooling environment. This continuous gas flow is dominated by an inert gas like N_2 with a relatively small quantity of waste streams (dilute streams).

Since the TGA analyser operates only with gaseous reactants to use waste streams from the identified list of liquid solvents, an additional system for the reactant delivery to the TGA was developed using Owlstone V-OVG. Figure 4 outlines the overall TGA-Owlstone setup.

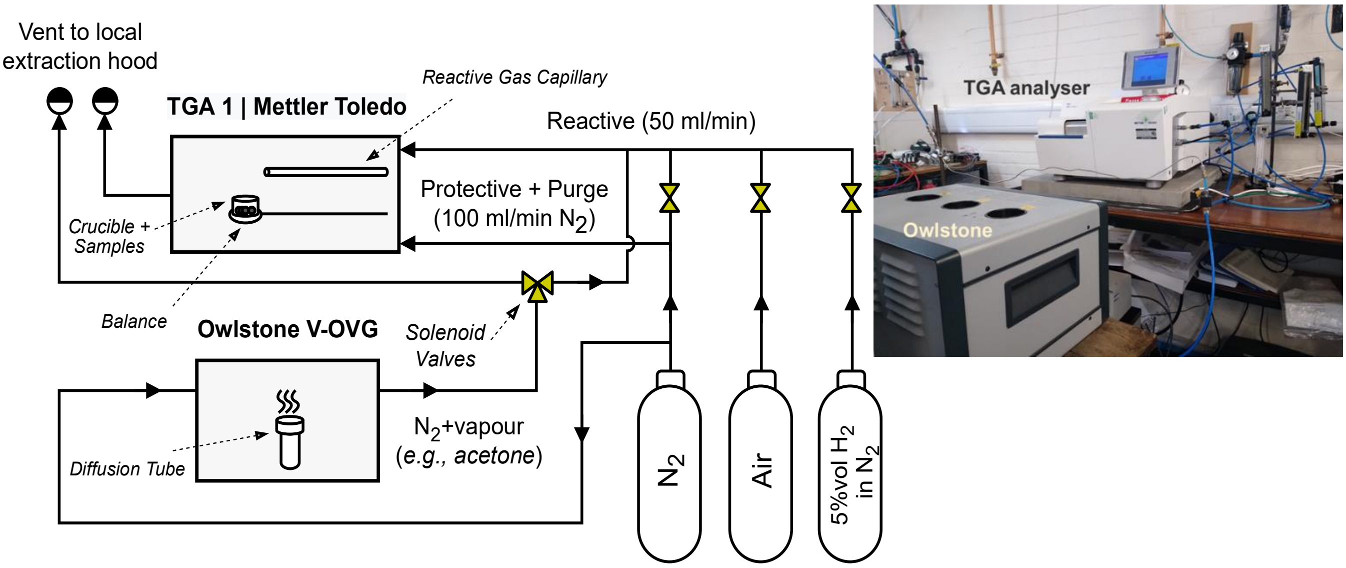


Figure 4 TGA-Owlstone Setup Schematics

TGA-Owlstone setup unique features:

- Mass loss / gain of MO_x/MO_{x-1} during reactions,
- Temperature variations,
- Various reactants (waste streams, water, air, *etc.*),
- Gas analysis for H_2.

Exemplary results from TGA experiments are presented in Fig. 5. Here, we recorded how the mass of a sample of MOx changes during heating and cooling when exposed to waste streams and H_2O. Upon heating and exposure to a stream containing dilute ethanol, the sample of LaCaFeMn-oxide lost mass, indicating oxygen donation. During cooling in the presence of water vapour (~2vol%), the mass increased, indicating oxygen uptake and the corresponding water-splitting reaction (and H_2 production).

From such experiments, we assessed how MOx candidates react in the two steps of H2Upgrade, comparing materials and the reducing potentials of waste streams.

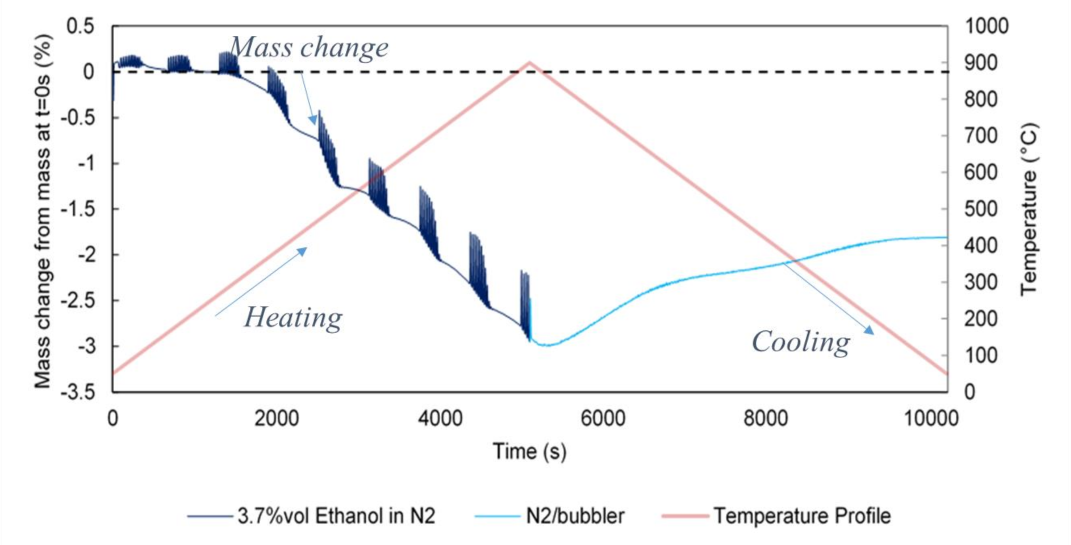


Figure 5 Mass profile of $La_{0.6}Ca_{0.4}Fe_{0.4}Mn_{0.6}O_3$ (the actual stoichiometry for O has not been confirmed). Reduction in 3.7%vol Ethanol in N_2 and reoxidation in humid N_2.

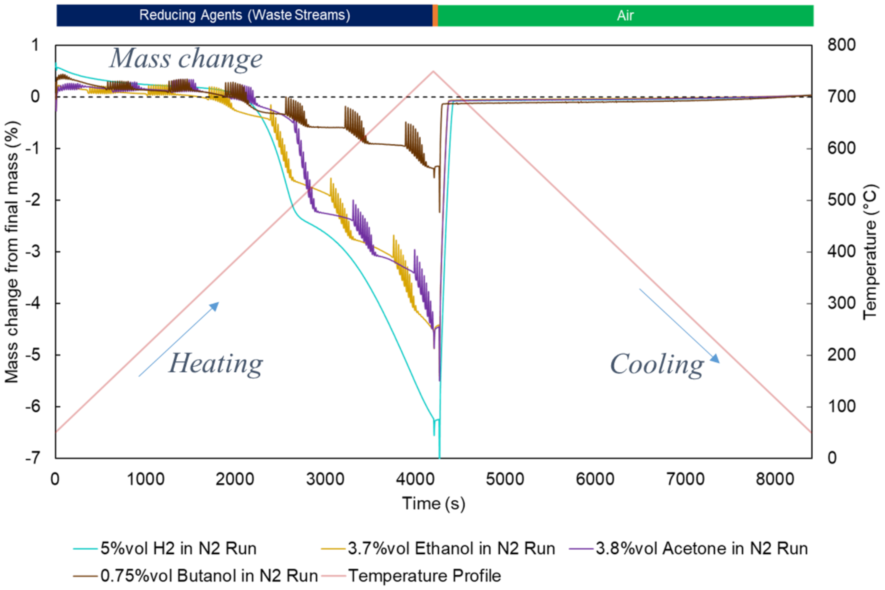


Figure 6 Mass profile of Fe_2O_3 on $Gd_{0.3}Ce_{0.7}O_2$. Reduction in various waste streams (navy blue region) as labelled and reoxidation in air (green region).

Exemplary results for reduction with different dilute waste streams are shown in Fig. 6. As expected, ethanol and acetone, which both contain one atom of oxygen in the molecular structure, have a similar reducing potential; thus, the final mass of MOx in both experiments was similar.

The same experiments were also conducted after connecting a hydrogen analyser at the outlet of the TGA-Owlstone reactor. This way, we measured the H_2 production, correlating it to the mass gain of MOx when it splits water. Exemplary results are given in Fig. 7.

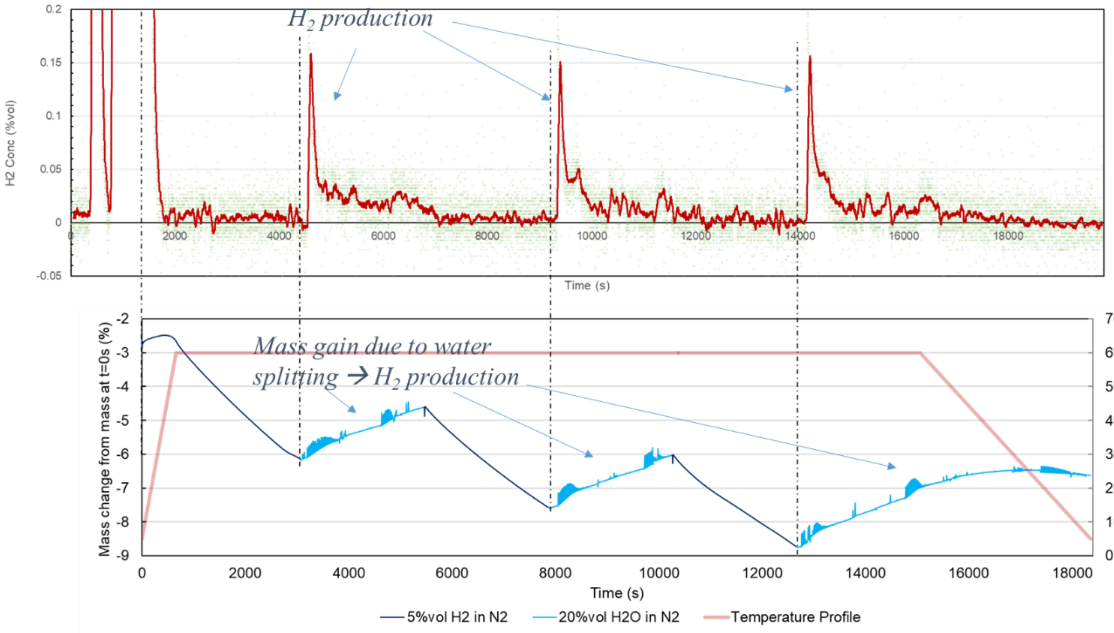


Figure 7 H_2 Production using Fe_2O_3 on $LaFeO_3$.

3.6.2. Experiments in a packed-bed reactor (PBR)

A packed-bed reactor has been designed and constructed in the project to conduct experiments with an increased amount of MOx materials. Schematics are provided in Fig. 8. The main reactor was constructed from a stainless-steel tube (15 mm i.d.) mounted into an electrically-heated furnace. Experimental temperature is set up using a PID controller against a temperature reading from a thermocouple positioned in the middle of the MOx bed. Gases are fed to the main reactor from the top. After the reactor, the gas stream is directed to an analyser. Gas flowrates are controlled with mass-flow controllers and rotameters. Step 1 and step 2 of the H2Upgrade cycle are set up with a programme that controls the delivery of gases to the reactor using solenoid valves. For step 1 – reduction of MOx with waste streams, either selected waste streams were used or a dilute mixture of CO in N_2. For step 2 – reoxidation of MO_{x-1}, either H_2O was delivered for water splitting, CO_2 for splitting to CO, or air for full reoxidation to the original MO_x.

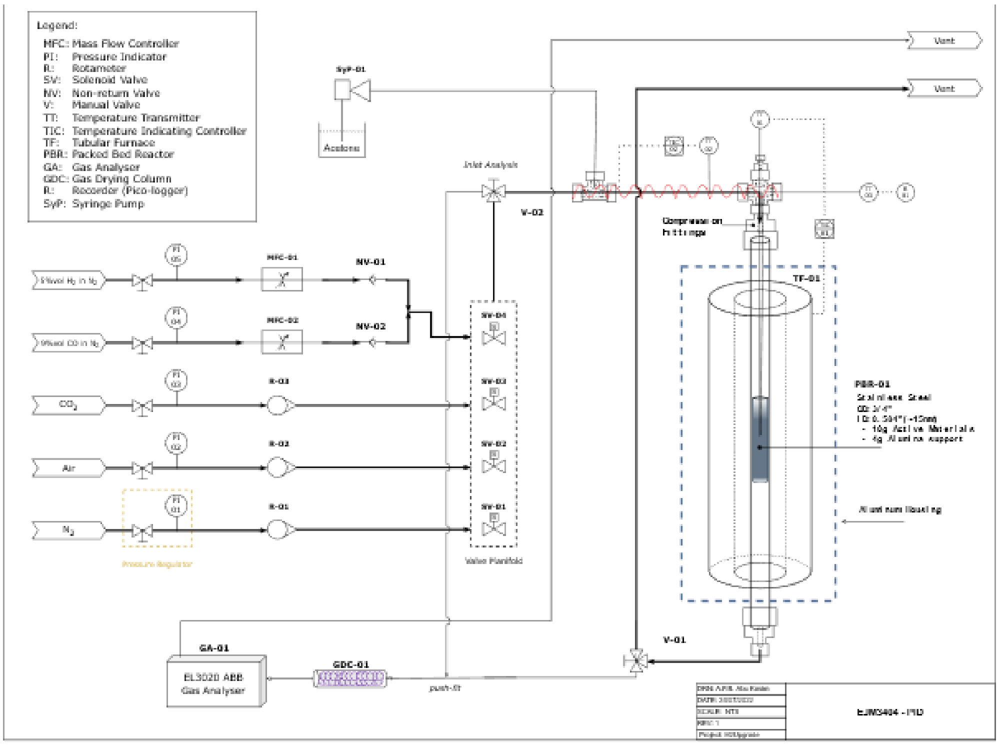


Figure 8 PBR setup for experiments with 10 g of MOx materials.

PBR setup unique features:

- Experiments with 10 g of MOx materials,
- Low-medium-high flowrates possible,
- High concentrations of reactants – up to 100vol%,
- Gas analysis for H_2.

Gas profiles from one of the PBR experiments are presented in Fig. 9. Here, we used a composite material based on a perovskite and Fe_2O_3. The results show the two steps of H2Upgrade with Step 1 performed using CO to react with MO_x, producing CO_2, and Step 2 performed reversing this reaction, *i.e.* exposing MO_{x-1} to CO_2 and producing CO. Those results allow us to assess how much H_2 can be produced during step 2 with pure water vapour.

Further experiments when water was used are presented in Fig. 10. Here, we applied three steps to observe whether the water-splitting step allowed the material to oxidise to the maximum possible state. Thus, in step 1, MOx particles reacted with CO; in step 2 – they were exposed to water; thus, we measured H_2, and then in step 3 – they were exposed to CO_2. Adding the last step showed that water splitting was not finished and could have been carried for longer or in a higher concentration of H_2O.

Importantly, from the PBR experiments, we were able to establish the amount of H_2 that can be produced from a unit mass of MOx material. Those results were essential for the first-pass design of an H2Uprage unit, determining the ballpark of the required amount of material per reactor.

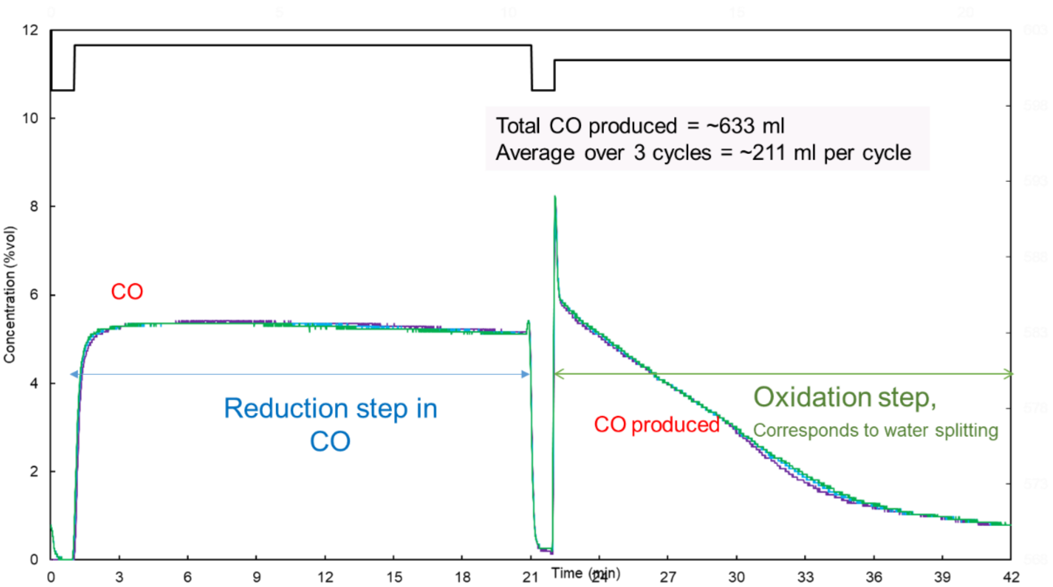


Figure 9 Results from the PBR experiments showing two steps of H2Upgrade for CO oxidation and CO_2 splitting.

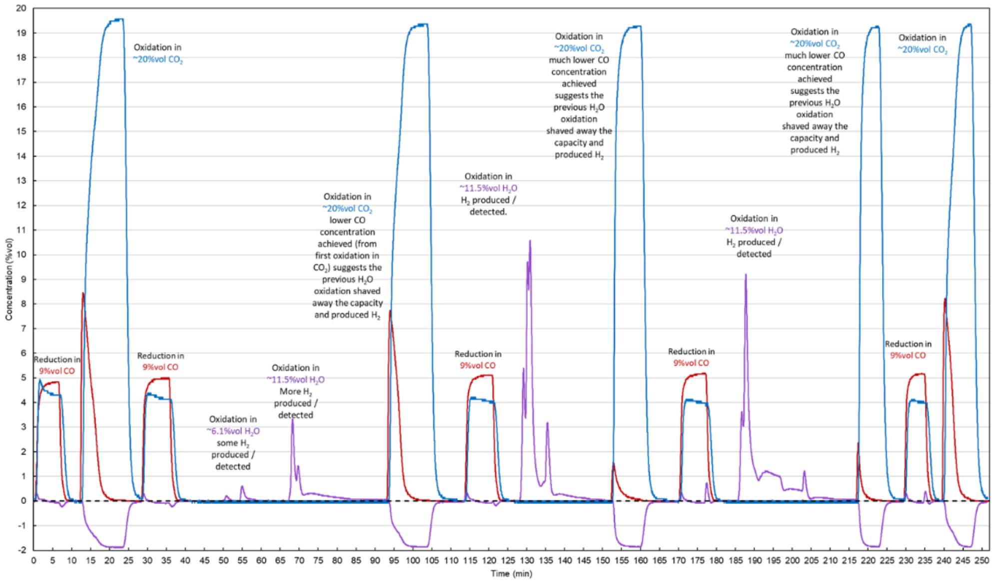


Figure 10 Gas profiles from PBR experiments with three steps: Step 1 – reduction in CO, Step 2 – water splitting (production of H_2), Step 3 – oxidation in CO_2. Negative values for H2 during oxidation in CO2 are artefacts from the crossensitivity of the H_2 analyser to CO_2.

In Fig. 10, for investigating water splitting with high concentrations of H_2O, water was injected into the reactor using a small tube (1/8 inch stainless steel) inserted through one of the thermocouple ports. Figure 10 presented the results from those experiments, demonstrating that the achieved concentration of H_2 exceeded >10%vol$_{H2}$ (following water removal through the gas drying column) with no other products detected, outlining that pure H_2 is obtainable when pure steam is used in the reoxidation step.

The overall yield is also consistent with what was obtained in Fig. 9, which is approximately 1) 120 ml of CO, 2) 30 ml of H_2 + 100 ml of CO, 3) 120 ml H_2 + 14 ml of CO, 4) 113 ml of H_2 + 12 ml of CO, and 5) 100 ml of CO. Thus, the average production capacity of CO or H_2 was ~120 ml or 12 $ml_{product}/g_{material}$ capacity. Clearly, water splitting was feasible, and the problem in experiments with low H_2 yields came from the problematic water delivery.

3.7. Environmental and risk assessment

3.7.1. Life-cycle analysis of H2Upgrade units

With the first-pass design of the H2Upgrade Technology performed, the environmental assessment of the overall system was initiated. The environmental impact of a unit of the H2Upgrade system was analysed following a Life-cycle Assessment (LCA) approach. LCA is a technique used to assess the environmental impact associated with all stages of a "product or process" (*i.e.* the H2Upgrade technology), from the extraction of raw materials to the disposal or end of life.

Since H2Upgrade uses waste streams, a potential environmental benefit arises from utilising those streams rather than disposing of or incinerating them. In Section 3.1, the "Incineration" fate with the "Spent Solvent" waste-stream category was discussed, following the topology of the Waste Data Interrogator[2–4]. Thus, a suitable comparison could be attained when comparing the H2Upgrade process with waste incineration using extractable thermal energy as the reference product. Treating H_2 as the main product, electrolysis would be a more appropriate comparison. But all three (H2Upgrade, electrolysis, incineration) can be easily unified on the bases of extractable thermal energy, e.g. as was presented for electrolysis earlier in the literature. Results give the global warming potential (in $gCO_{2,eq}/MJ$) and other LCA parameters in Figs. 11 and 12. From the compared technologies, neither assumes CCS, as the scale of H_2 production is small. However, in H2Upgrade, the produced CO_2 is pure and ready to use in the food industry, thus, can be used as a sellable product. Thus, for H2Upgrade our analysis in Fig. 11 shows CO_2 emissions from the whole lifetime the installation, divided into two cases: with CO_2 sold as a product (blue bars), and with CO_2 from step 1 of the process released (additional emission depicted with orange bars). Our business plan assumes that CO_2 will be sold.

From this preliminary environmental assessment, the key takeaways are summarised as follows (assuming CO_2 in H2Upgrade is captured and sold):

- The environmental impact of producing heat from H_2 generated first using industrial solvents in H2Upgrade, decreases by 63% compared to producing an equivalent amount of thermal energy *via* waste solvent incineration.

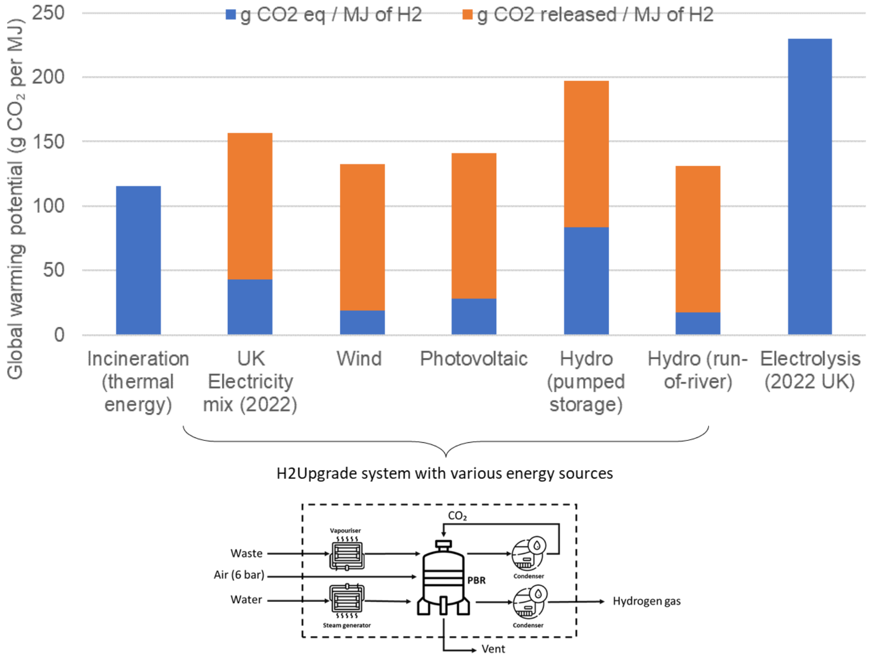


Figure 11 Global warming potential comparison of the H2Upgrade technology between different energy sources. Blue – represents all lifetime emissions – for H2Upgrade assuming CO2 from step 1 of the process is sellable, Orange – additional CO_2 emissions if CO_2 is not sold but released.

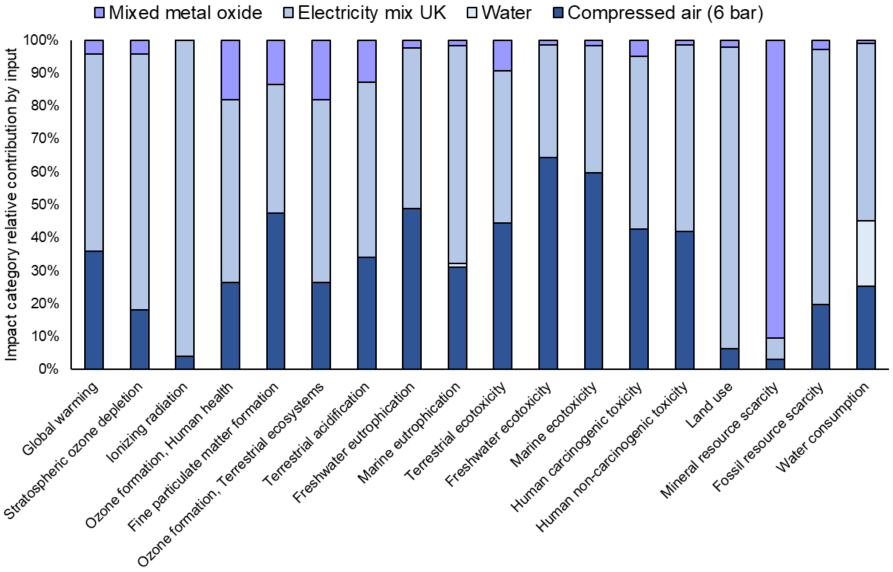


Figure 12 Overall environmental impact assessment of H2Upgrade.

- ➢ With the current UK electricity mix, the H2Upgrade approach to hydrogen production emits about 80% less greenhouse gas compared to electrolysis.

3.7.2. First pass designs – considerations of explosive risks for new devices

New devices working with explosive substances can only be allowed on the market if they comply with ATEX directives. Those are two EU directives on workplace and equipment used in explosive atmospheres: Appareils destinés à être utilisés en ATmosphères EXplosibles (French for "Equipment intended for use in explosive atmospheres").

ATEX is a specialised area requiring detailed knowledge of the industry's best practices and current regulations. Thus, we contacted two companies, Hornbill Ltd and ATEX Explosion Hazards Ltd, to discuss how full risk assessments would look and how they are commonly arranged. Our main conclusion from those meetings was that a full ATEX assessment would be required before commercialising H2Upgrade units and that our units would need to comply with the 'Equipment' Directive (2014/34/EC), which applies to all equipment used in explosive atmospheres including protective systems. Working with H_2 (gas group IIC) would require ATEX Zone 0, suitable for systems where explosive hazards are always present. This means that Safety Category 1 for all equipment will be required.

4. Benefits and barriers

Commercial benefits of H2Upgrade are not only in the efficient and inexpensive technology for expanding the current portfolio of possible H_2 production methods, but additionally, H2Upgrade provides an urgently needed solution to waste management, utilising streams, which otherwise would be either flared (waste) or would require purification and neutralisation (costly). Hence, besides producing H_2, H2Upgrade can prevent the emission of hydrocarbons that have greenhouse gas warming potential tens to hundreds of times higher than CO_2. For example, utilising only landfill gas in the UK, the avoided emissions will be equivalent to ~19 MtCO_2equivalent[12] (assuming that landfill gas is otherwise released into the atmosphere), with further savings from the produced H_2 that would substitute other energy sources.

A possible demonstration of H2Upgrade is graphically presented in Fig. 13.

Key benefits of the H2Upgrade technology are:

- Transformation of no-cost, low-value waste streams into high-value concentrated H_2 streams.
- Acceleration of the hydrogen economy – H_2 production will become attractive to waste producers, with H_2 ready to use on-site or injected into the NG/H_2 grid.
- Waste management – avoiding costs of purification and neutralisation of waste streams.
- Significant reduction of GHG emission when using the produced CO_2 as a product, and avoidance of emissions if using alternative technologies.
- Low CAPEX – delivering the first small-scale competition to electrolysers.
- Simplicity – delivering an efficient on/off technology realised in medium-scale units
- Mobility and flexibility of the H2Upgrade units – to offer waste management service compatible with various wastes.

- Reliability, maturity, scalability – the 2-step technology has been demonstrated from lab-scale to pilot-scale installations, and can be designed and scaled as modular installations.

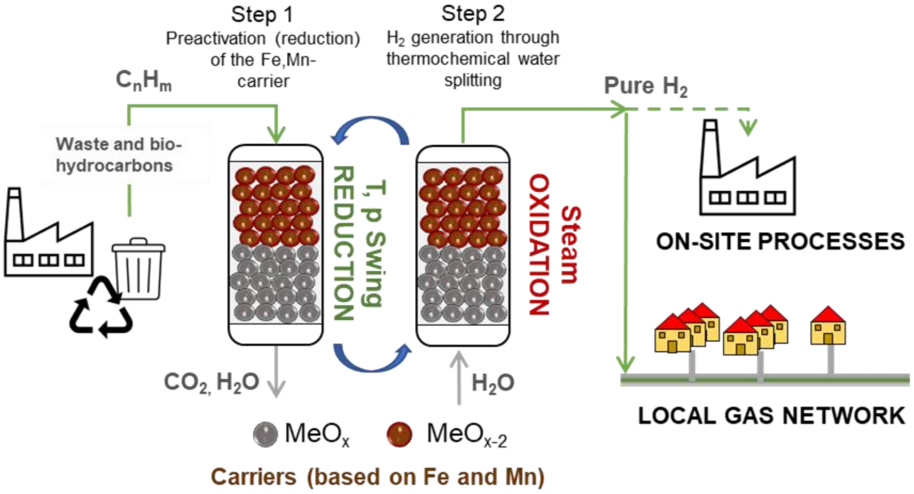


Figure 13 Possible implementation of H2Upgrade.

Potential technology implementation barriers:

- Difficult market entry with the well-established incumbent technology for methane-steam reforming.
- Lack of interest in H_2 from the small and middle-scale chemical industry, *e.g*. because of the lack of government incentives and the volatile market situation.
- Lack of interest in CO2 from the food industry.
- Drop waste management and neutralisation costs.
- Lack of interest in greenhouse gas emissions from streams other than CO_2.

4.1. Levelized costs of hydrogen (LCOH) for H2Upgrade w/ and w/o CCS

The selected production capacity for H2Upgrade corresponds to H_2 production that can be obtained with 60-70 kW electrolysers. The cost of such systems for water electrolysis is min. ~£250k, accounting for water purification units.

(not described here) gave the For the analysis of levelised cost, we took 10 years of H2Upgrade unit operations and CAPEX and OPEX costs. Counterfactuals are shown in Table 3 and highlighted by the shaded cells.In this analysis we consider CO_2 as a possible sellable product, because after the removal of H_2O , the stream of CO_2 is pure. We analysed the levelised costs from two perspectives:

- "waste to H_2"-perspective – In such a case, waste streams are purchased, but the CO_2 is a sellable product, with the selling price taken as a 2020 market price.Here, the LCOH varies between £3.25/kg and £9.94/kg, depending on the level of heat integration achieved in H2Upgrade. We consider the lowest LCOH results, £3.25/kg, more realistic as it uses excess heat to drive reactions.

- "customer"- perspective – where customers are also waste-producers.They profit from selling CO_2 and from savings from avoided solvent disposal costs. Solvent disposal costs are significant, and these savings can make the process cost-neutral and even a net revenue generator. This leads to costs as low as -£3.49/kg, *i.e.* the system has become a cheaper way of disposing of solvent whilst also producing H_2.

Table 3. Results of the LCOH analysis for H2Upgrade2.0 with CO2 used as a sellable by-product

	Waste to H_2 producer			Customer perspective				
	Base case	Partial heat integration	Full heat integration	Base case	High CO_2	Waste saving	Full heat integration	FHI+waste saving
CO_2 price (£/kg)	0.2	0.2	0.2	0.2	1	0.2	0.2	0.2
Power price (£/kwh)	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
Fuel price (£/kg)	0.2	0.2	0.2	-0.2	-0.2	-1	-0.2	-1
CO_2 revenue	£243,630	£243,630	£243,630	£243,630	£1,218,150	£243,630	£243,630	£243,630
Power Cost	£457,340	£286,131	£0	£286,131	£286,131	£286,131	£0	£0
Fuel cost	£111,730	£111,730	£111,730	-£111,730	-£111,730	-£558,652	-£111,730	-£558,652
OM cost	£144,000	£144,000	£144,000	£144,000	£144,000	£144,000	£144,000	£144,000
Capital cost	£210,000	£210,000	£210,000	£420,000	£420,000	£420,000	£420,000	£420,000
Levelised costs								
£ per kg H2	£9.94	£7.44	£3.25	£7.24	-£7.02	£0.70	£3.05	**-£3.49**
£ per MWh LHV H2	£296	£222	£97	£216	-£209	£21	£91	**-£104**
£ per MWh HHV H2	£250	£187	£82	£182	-£177	£18	£77	**-£88**

An alternative analysis with CCS is given in Table 4. H2Upgrade produces purified CO_2, thus, cost for capture are 0. However, we do not liquify CO_2, thus, this cost was finally added in the analysis, taking an average cost for CO_2 capture from CH_4 combustion, of $76/tonne [13]. Adding average costs of transport $11/tonne, and sequestration $10/tonne [13], brings the costs of CCS for H2Upgrade at $97/tonne, equivalent to £0.09/kg CO_2.This means that after heat integration in Phase 2, the cost of H_2 production from the perspective of waste-producers would be £8.22/kgH_2 but decreases to £5.15/kgH_2 when we decrease the price of the H2Upgrade unit to £210k, as proposed in Table 4. The technology still brings significant net gains if waste neutralisation is treated less conservatively than in our base-case scenario, *i.e*. at £1/kg.

Table 4. Results of the LCOH analysis for H2Upgrade2.0 with CCS

	Waste to H_2 producer			Customer perspective				
	Base case	Partial heat integration	Full heat integration	Base case	High CO_2	Waste saving	Full heat integration	FHI+waste saving
CO_2 price (£/kg)	-0.09	-0.09	-0.09	-0.09	0	-0.09	-0.09	-0.09
Power price (£/kwh)	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
Fuel price (£/kg)	0.2	0.2	0.2	-0.2	-0.2	-1	-0.2	-1
CO_2 revenue	-£109,633	-£109,633	-£109,633	-£109,633	£0	-£109,633	-£109,633	-£109,633

Power Cost	£457,340	£286,131	£0	£286,131	£286,131	£286,131	£0	£0
Fuel cost	£111,730	£111,730	£111,730	-£111,730	-£111,730	-£558,652	-£111,730	-£558,652
OM cost	£144,000	£144,000	£144,000	£144,000	£144,000	£144,000	£144,000	£144,000
Capital cost	£210,000	£210,000	£210,000	£210,000	£210,000	£210,000	£210,000	£210,000
Levelised costs								
£ per kg H2	£9.34	£7.73	£2.80	£9.34	£7.73	£2.80	£5.15	-£1.39
£ per MWh LHV H2	£278	£230	£83	£278	£230	£83	£153	-£41
£ per MWh HHV H2	£235	£195	£70	£235	£195	£70	£130	-£35

4.2. Purity of H_2

The outlet gas from the process will contain only H_2 and moisture, but the latter will be removed with a chiller drier (up to the dew point of -20°C, corresponding to 422 ppm of water), then using molecular sieve-based drying cartridges. The resulting purity of H_2 from H2Upgrade will be 99.999%.

4.3. Greenhouse gases mitigated, and potential H_2 production capacity

For the assessment of those two parameters, we have assumed that H2Upgrade units will be successfully commercialised, following the pathway and selling history of GR2L's Argon0 units. Namely, we expect the rollout of the technology to lead to 500 sold H2Upgrade units in 5 years. Assuming the upper limit for the planned production per unit, namely 10 Nm^3H_2/h, gives:

- Averaged requirement of tonnes of waste: 56 t/year per H2Upgrade unit. Assuming that all this waste would correspond to equivalent CO_2 emission means that 500 units of H2Upgrade would help mitigate 84 MtCO_2/year. This calculation assumes that waste would otherwise be incinerated, releasing 84 MtCO_2/year to the atmosphere, while the user of H2Upgrade sells CO_2 as a product.
  Another basis for comparison is MJ of useful thermal energy accumulated (See our LCA analysis). Then, the savings in CO_2 emissions from the production of H_2 referred to 500 units of H2Upgrade would be 67 MtCO_2/year compared to incineration and 62 MtCO_2/year compared to H_2 from electrolysis. The first number is lower than 84 MtCO_2/year because of the assumption that heat from incineration can be used.
- total production capacity of 500 H2Upgrade units: 43.8×10^6 m^3 H_2/year. This production capacity translates to 0.12 TWh/year LHV.

The H_2 production capacity will grow with time after commercialisation and multiply accordingly with the number of H2Upgrade units being operational at customer sites.

5. Phase 2 - development plan

Our plan for the Phase 2 project is to modify one of the GR2L's current commercial units used in the purification of argon: Argon0. The required modifications include heat integration of two CLC reactors, compatibility of materials with H2 and possibly increased pressures, and addition of vaporisers for H_2O and wastes. By modifying Argon0, we will be in a position to demonstrate scaled-up production of H_2 via H2Upgrade technology quickly (after the first 6 months of the Phase 2 project). This will also give us an opportunity to learn about any engineering challenges (e.g. full heat integration, continuous operations) of the large-scale process. After operating this demonstrator, we will design, build and deploy at a partner site a larger-scale pilot unit (after 15-18 months of the Phase 2 project). The deployment will be scheduled for 6 months to give a good overview of the operations under industrial conditions.

Total costs of H2Upgrade Phase 2: £1,907k (UCAM £1,037k, GR2L £870k). All UCAM costs have been assessed using the University costing tool (X5). Importantly, all GR2L's costs have been assessed based on the current operational costs.

6. Rollout potential

Our plan for rollout will follow GR2L's experience in the rollout of the Argon0 Argon Recycle units, which were introduced to the market in 2012. Assuming a similar level of success, we aim to have 500 H2Upgrade units sold globally over 5 years.

In the UK, we assess the rollout potential based on the amount of available waste. As we concluded from Section 3.1, waste streams that will be attractive to H2Upgrade are currently managed by incineration in the amount of 26,000 t/y. Assuming 30% of those streams diverted into H_2 production would result in 7,800 t/y of waste processed in 140 H2Upgrade units for H_2 production, equivalent to 0.03 TWh/year.

Our assessment for the total potential of H2Upgrade units globally is 10 times that in the UK over the 10-15 years of selling the nominal H2Upgrade units. That scales the number of sold units to 1400 and the H_2 production equivalent to 0.32 TWh/year.

Our main H2Upgrade unit will have a production capacity of 5-10 Nm^3 H_2/h, but during the first five years from commercialisation, we will also map another potential market for smaller scale production, 1-2 Nm3 H_2/h. Those units would be attractive to small-scale producers of waste streams, possibly interested in on-demand H_2 production or waste disposal rather than the continuous process we are currently developing. Assessing this potential could lead to selling smaller H2Upgrade units or creating services.

With the successful deployment of 5-10 Nm^3H_2/h units, we will also approach scaling the technology up to 50 Nm^3H_2/h and introducing it to large-scale industry. Our first market will be producers of bio-diesel *via* the HVO route. Those plants use H_2 to hydrogenate vegetable oils but also produce a waste product, propane. With H2Upgrade, those plants would be able to use this waste propane to produce bio-H_2 in-house. We will treat H2Upgrade units as modular technology, providing larger production capacities by multiplying the number of modules.

7. Route to market assessment

To enter the market, we will set up a new company as a joint venture between GR2L and the University of Cambridge. For that, we have support and mechanisms in place from

Cambridge Enterprise, which supports spin-outs and commercialisation of our research-originating activities. This support includes seed funding, contact with venture capitalists, a dedicated project manager, and IP protection.

Similarly, GR2L's experience in commercialising technologies based on chemical looping reactions with MOx is invaluable and gives the H2Upgrade team a significant advantage. With GR2L as the commercialisation partner, we will access their increasing global sales force in all key European territories and countries dedicated to green solutions.

Following the successful deployment of an H2Upgrade unit in Phase 2 NZIP project, our production of H2Upgrade units will be first based on the production routes of GR2L's for Argon0 Argon Recycle units. Those Argon0 units will be modified in the Phase 2 project and scaled up but staying within the current production potential of GR2L. We assess our starting production base as 12 H2Upgrade units built simultaneously in up to three months, giving 48 units produced in the first year. GR2L's current production capacity is approx. 25 units per month of their Argon0 Argon Recycle system, with sales going mostly into the solar PV and semiconductor chip supply chains.

To reach the planned rollout of 500 units sold in the first 5 years, the starting production capacity would be scaled up to 115 units per year at the end of the first year of commercial activities. This will be possible by building a new production line with first-round funding from venture capital.

Job creation

Our new company will hire 4 people in the first year, and another 4 in the second year. Jobs will also be created across the whole supply chain, especially in the subcontractors of elements to the H2Upgrade units. GR2L works with ~ 10 subcontractors. We estimate that our new company can reach about 40% of GR2L's production capacity in two years of operation, which would result in the creation of 10 jobs in subcontractors (1 per subcontractor). Each of the sold H2Upgrade units will create jobs in customers' companies. We expect they can hire 0.5 person per H2Upgrade unit, after saving on the waste disposal fees and H_2 purchase costs.

Carbon savings

Carbon savings for the UK after selling 140 H2Upgrade units have been assessed as 23.5 $MtCO_2$/year, and after selling 500 units in the first 5 years, as 84 $MtCO_2$/year.

8. Dissemination

Dissemination of the project results and the potential of the technology has been undertaken throughout the whole project and will extend beyond its end date.

The activities include:

- Engagement with the academic community during the ChemEngDay UK 2022 at University College London (04/2022) and International Chemical Looping Conference in Zaragoza (09/2022),

- Presentation at the University of Cambridge, CEB – dissemination of project goals (04/2022),
- Direct engagement with stakeholders (contacts and discussions with ~20 companies working in H_2 production, waste management, chemical industry, engineering processes, risk assessment, catalyst manufacturing, *etc.*),
- Discussions on future collaborations with other consortia from Phase 1,
- Presentation of the project and main findings at the International Conference on Energy Storage in Birmingham (10/2022),
- Project advertising through communications on the CEB website and LinkedIn.
- Meetings and calls with potential stakeholders.

9. Conclusions

H2Upgrade offers an attractive technology to valorise waste into high-value H_2. During the Phase 2 project, the technology will reach TRL8-9, ready for commercialisation. This report demonstrates that the process can be very attractive to waste producers if they are interested in H_2 production.

References

(1) Luo, M.; Yi, Y.; Wang, S.; Wang, Z.; Du, M.; Pan, J.; Wang, Q. Review of Hydrogen Production Using Chemical-Looping Technology. *Renew. Sustain. Energy Rev.* **2018**, *81*, 3186–3214. https://doi.org/10.1016/j.rser.2017.07.007.

(2) Agency, E. *2020 Waste Data Interrogator*. https://www.data.gov.uk/dataset/bb40d091-a346-4b75-aa54-df7d347bed93/2020-waste-data-interrogator (accessed 2022-09-06).

(3) Gov.UK. *Classify different types of waste*. GOV.UK. https://www.gov.uk/how-to-classify-different-types-of-waste (accessed 2022-09-06).

(4) Environment Agency. *Waste Classification* | *Guidance on the Classification and Assessment of Waste*; 2021.

(5) Seyler, C.; Capello, C.; Hellweg, S.; Bruder, C.; Bayne, D.; Huwiler, A.; Hungerbühler, K. Waste-Solvent Management as an Element of Green Chemistry: A Comprehensive Study on the Swiss Chemical Industry. *Ind. Eng. Chem. Res.* **2006**, *45* (22), 7700–7709. https://doi.org/10.1021/ie060525l.

(6) Nemeth, B.; Lang, P.; Hegely, L. Optimisation of Solvent Recovery in Two Batch Distillation Columns of Different Size. *J. Clean. Prod.* **2020**, *275*, 122746. https://doi.org/10.1016/j.jclepro.2020.122746.

(7) Chea, J. D.; Lehr, A. L.; Stengel, J. P.; Savelski, M. J.; Slater, C. S.; Yenkie, K. M. Evaluation of Solvent Recovery Options for Economic Feasibility through a Superstructure-Based Optimisation Framework. *Ind. Eng. Chem. Res.* **2020**, *59* (13), 5931–5944. https://doi.org/10.1021/acs.iecr.9b06725.

(8) Rinner, M.; Kind, M.; Schlünder, E.-U. Separated Solvent Recovery from Waste Gas with Cryo-Condensation. *Sep. Purif. Technol.* **2002**, *29* (2), 95–104. https://doi.org/10.1016/S1383-5866(02)00065-5.

(9) McCann, T.; Marek, E. J.; Zheng, Y.; Davidson, J. F.; Hayhurst, A. N. The Combustion of Waste, Industrial Glycerol in a Fluidised Bed. *Fuel* **2022**, *322*, 124169. https://doi.org/10.1016/j.fuel.2022.124169.

(10) *Hydrogenation | Chemical Manufacturer | Robinson Brothers*. https://www.robinsonbrothers.uk/chemistry-competences/hydrogenation (accessed 2022-09-12).

(11) Wang, X.; Gao, Y.; Krzystowczyk, E.; Iftikhar, S.; Dou, J.; Cai, R.; Wang, H.; Ruan, C.; Ye, S.; Li, F. High-Throughput Oxygen Chemical Potential Engineering of Perovskite Oxides for Chemical Looping Applications. *Energy Environ. Sci.* **2022**, *15* (4), 1512–1528. https://doi.org/10.1039/D1EE02889H.

(12) 2019 UK Greenhouse Gas Emissions, Final Figures. **2019**, 42.

(13) Schmelz WJ, Hochman G, Miller KG. Total cost of carbon capture and storage implemented at a regional scale: northeastern and midwestern United States. Published:14 August 2020https://doi.org/10.1098/rsfs.2019.0065