Hydrogen BECCS Innovation Programme: Phase 1

Novel Biohydrogen Technology: Hydrogen by Aqueous- Reforming of Organic Wastes (HAROW)

PUBLIC REPORT

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1 Introduction

Hydrothermal reforming of high-moisture biomass feedstocks is an effective technology for hydrogen production from various types of wet biomass feedstocks, either directly, or via a mild-temperature hydrolysis process to organic-rich feed stream for conversion into hydrogen. The technology offers the unique opportunity for the utilisation of various wet low-grade biogenic organic aqueous streams such as Anaerobic Digestion (AD) digestate, crude glycerol, aqueous fractions (process waters) from pyrolysis, and hydrothermal liquefaction of biomass, microalgae and macroalgae as well as food wastes with the dual benefit of a cleaner water output.

Essentially the output from the aqueous phase reforming process generates methane, carbon dioxide and hydrogen, and the methane can then be steam reformed to generate carbon dioxide and hydrogen. Our innovation (HAROW) is that the two reactions are combined in a single process to operate at an intermediate temperature, and there is sufficient carry over of water from the aqueous-phase reforming process to steam reform the methane. Earlier experimental work conducted at Aston University showed that some 800 mg CH_4/gC can be produced from crude glycerol at 95% conversion at temperatures between 350 and 500 °C and pressures of up to 250 bar. Therefore, applying typical conversion of methane during steam reforming (90%), the yield of hydrogen can reach 374 mg H_2/gC in the feed.

The objectives of the HAROW project are to demonstrate that both reactions can be combined in a single process, and will work effectively, producing high yields of biogenic hydrogen using abundant “dirty” aqueous waste streams (e.g., crude glycerol, AD digestate and other biogenic organic materials). The arising CO_2 could be captured by a number of techniques, but the novel application of Starbons® (a mesoporous carbon-based adsorbent material) has been tested in this project.

2 Detailed technical description

HAROW is based on using a combination of thermo-catalytic processes to produce hydrogen, and more specifically in hydrothermal reforming using water as the active hydrogen source[i]. Reforming of biomass-derived chemicals is generally classified by the reaction conditions, in particular, by the water phase, namely steam phase reforming (SPR), aqueous phase reforming (APR) and supercritical water reforming (SCWR)[ii].

The investigated pathway of the present work is APR. Biomass-derived oxygenated compounds such as glycerol, sugars, and sugar alcohols can be used to produce hydrogen by APR. The reaction is performed at low-to-medium temperatures and high pressures to ensure liquid phase processing. The effectiveness of this method depends critically on the implementation of new generations of heterogeneous catalysts, as well as process designs which improve the energy efficiency of the process. Catalytic aqueous phase reforming may prove useful in the near future for the generation of H_2-rich fuel gas from carbohydrates extracted from renewable biomass and, more interestingly, from biomass waste streams[iii]. The APR process can handle various types of wet biomass feedstocks either directly or via a mild-temperature hydrolysis process to organic-rich feed stream for conversion into hydrogen.

The hydrogen production pathway being investigated involves a three-stage process for conversion of crude glycerol to hydrogen. The first stage is the aqueous phase reforming (APR) of crude glycerol (approximate molecular formula: $C_8H_{16}O$; based on elemental composition) to form biomethane, and following the stoichiometric equation shown below:

$$C_8H_{16}O + 5H_2O \rightarrow 5CH_4 + 3CO_2 + 3H_2 \qquad (2)$$

Following the APR stage, the biomethane produced undergoes conventional steam reforming step to produce hydrogen as shown in equation (2). Simultaneously, water gas shift (WGS) occurs due to the co-existence of CO and H_2O in the gas phase as shown in equation (3). The overall stoichiometry of the investigated process for conversion of crude glycerol to hydrogen is then shown in equation (4).

$$5CH_4 + 5H_2O \rightarrow 5CO + 15H_2 \qquad (2)$$

$$5CO + 5H_2O \leftrightarrow 5CO_2 + 5H_2 \qquad (3)$$

$$C_8H_{16}O + 15\,H_2O \rightarrow 8\,CO_2 + 23\,H_2 \qquad (4)$$

It is common for a WGS to be performed after SPR, typically as a high temperature and then low temperature process.

Crude glycerol (CG) has been selected as an example feedstock for the current project. Biodiesel has been successfully used as an alternative low carbon fuel in the strategy to de-fossilise the transportation sector, and crude glycerol is obtained as a by-product of the biodiesel production. The ratio is 1kg of crude glycerol obtained per 10 kg of biodiesel produced. Using crude glycerol would help biodiesel industry and enhance waste management optimisation. Crude glycerol contains glycerine and other substances classified as Material Organic Non-Glycerol (MONG), which are oxygenated hydrocarbon sources derived from biomass also suitable to be converted to H_2 through the APR pathway. The used glycerol for this project is provided by Olleco (biodiesel producer), and the composition of this used glycerol is shown in the following table:

Component	Composition (% m/m)
Water	<20
Glycerol	>60
Ash	<10
MONG	10-15
Sulphur	<2
Methanol	<5

Table 1 Approximate composition of Olleco's crude glycerol (CG). MONG is "material, organic, not glycerol" – basically all the other organics present excluding methanol and glycerol.

Previous batch-based work at Aston University has shown the viability of the approach as shown in Figure 1.

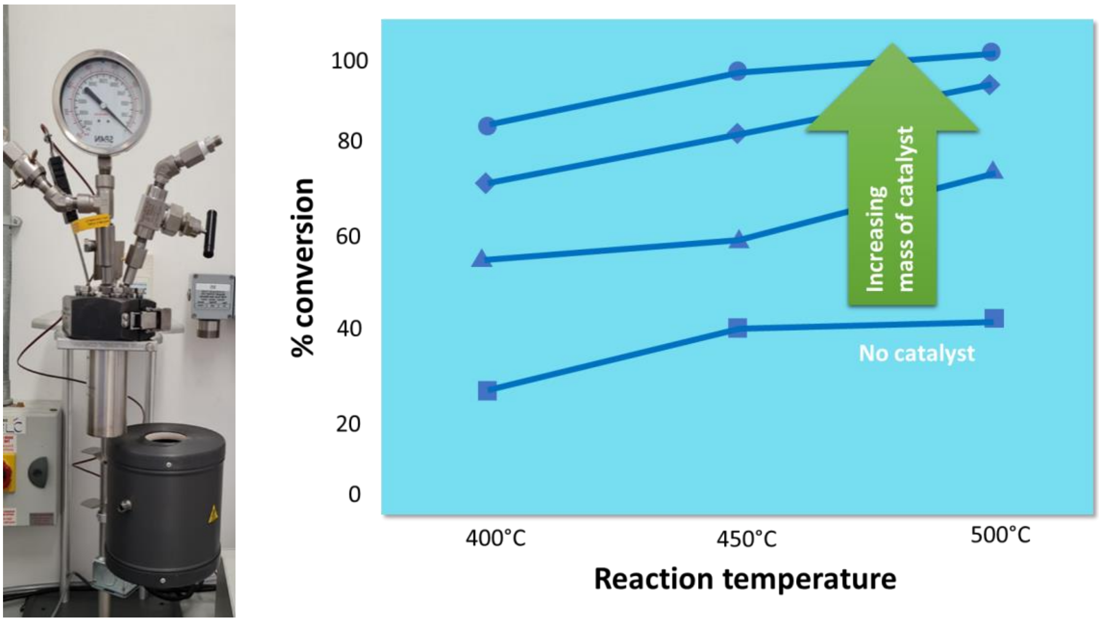


Figure 1 Aston's batch reactor and example data from some of their work. Feed: 15 wt% Bio-oil, Reactor type: Batch, Reaction time: 1h, Temperature: 400 °C – 500 °C

This project has involved the construction of a pilot scale Lab rig (Figure 3) allowing the process to be demonstrated in flow, and to check the kinetics in flow match the expectations from the previous batch studies.

Figure 2 Laboratory rig built during the HAROW project to measure the kinetics in flow of the aqueous phase reforming reactions.

Using the rig, samples of pure and crude glycerol were processed, initially to study the kinetics of the APR process. To summarise the results of the laboratory trials:

- Conversion of the organic content of the water is between 80 and 90%.
- Concentrations of hydrogen ~40% (volume %) have been achieved (Table 2), but this is with some residual hydrocarbons and carbon monoxide, which suggests that the SPR and MT-WGS were not entirely effective and there was not time to refine these processes within the project. With these processes refined, hydrogen volume concentrations >70% should be achieved.

The data from the laboratory trial was used to study the kinetics of the process in flow. The rates of the reaction for the 20 wt % glycerol solution were determined to be in the range $4.4 \times 10^{-4} – 10.3 \times 10^{-4}$ mol g^{-1} min^{-1}. This is between 5-10x faster than anticipated.

Component	**C_xH_y**	**H_2**	**CO**	**CO_2**
Volume %	19%	40%	13%	29%

Table 2 – Average composition based on 3 runs of the full HAROW system

The data from the laboratory trials shows the process works and would be scalable. Indeed, the differences between batch processing (Aston's original work) and continuous operation (HAROW) have become more apparent, and there are clear stoichiometric efficiency and operational benefits from the latter. Further work on process optimisation should be done, which is expected to improve the overall outcome; even without additional data there is nothing to suggest the process would not be viable.

Based on the background science and the kinetics experiments, a concept design was developed, including sizing of the various heat exchangers. A process design report was prepared based on the concept design for the scale up of the process and the P&ID prepared.

The design is based on mixing anaerobic digestate and crude glycerol to get the right concentration of organic material; so, there are 2 feedstocks and a mixing tank.

To further improve the energy efficiency, an energy recovery system will be included.

It is estimated that the system will produce around 450 mol/hr of hydrogen, or 0.9 kg/hr of hydrogen produced at the end of the systems cycle. CO_2 capture will be achieved with a solid adsorbent in a pressure swing followed by compression and storage.

3 Carbon Lifecycle Assessment of the technology

The Carbon Life Cycle assessment has been based on the experimental data generated. The boundary of the assessment is shown in Figure 3.

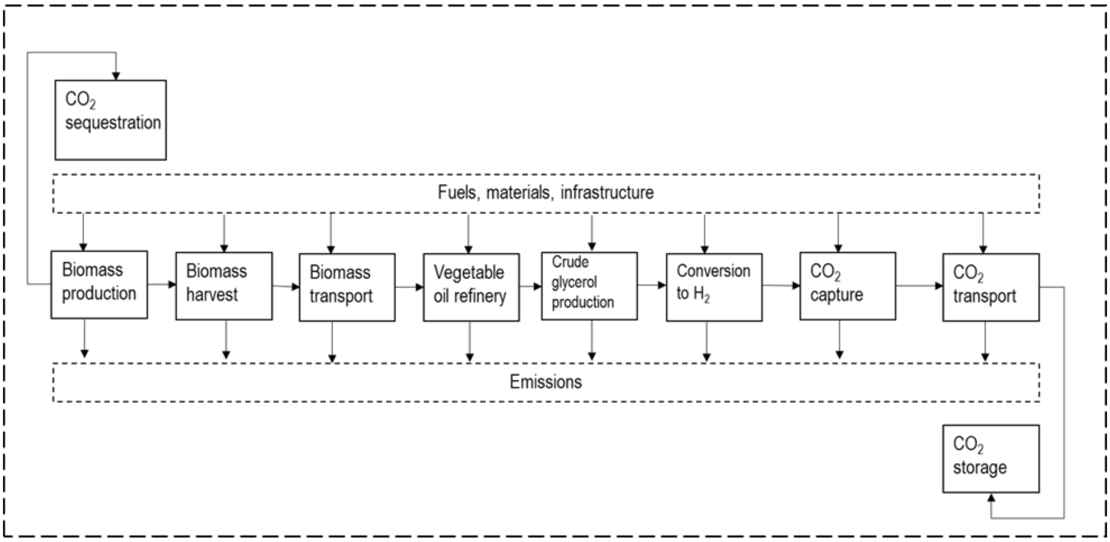


Figure 3 – Boundary for the carbon lifecycle analysis

The results show that the net CO_2 emissions from the process equals -2.15 $kgCO_2e$ per kg of H_2 produced; this value takes into the account the CO_2 sequestration obtained from growing the biomass used for production of the crude glycerol feedstock. The net total emissions recorded excluding CO_2 sequestration from biomass growth to produce crude glycerol is 11.3 $kgCO_2e$ per kg of H_2 produced. The emissions directly associated with crude glycerol conversion to hydrogen is 7.9 $kgCO_2e$ per kg of H_2.

4 Detailed Engineering Design for Demonstration Project

Detailed engineering calculations were completed to determine the sizing of major components. A 3D model was then prepared as shown in Figure 4. Additional images are shown in Appendix A. The footprint, excluding the cooling tower and the 8 ft shipping container is that of a 20 ft shipping container and could produce 15 T/yr of hydrogen.

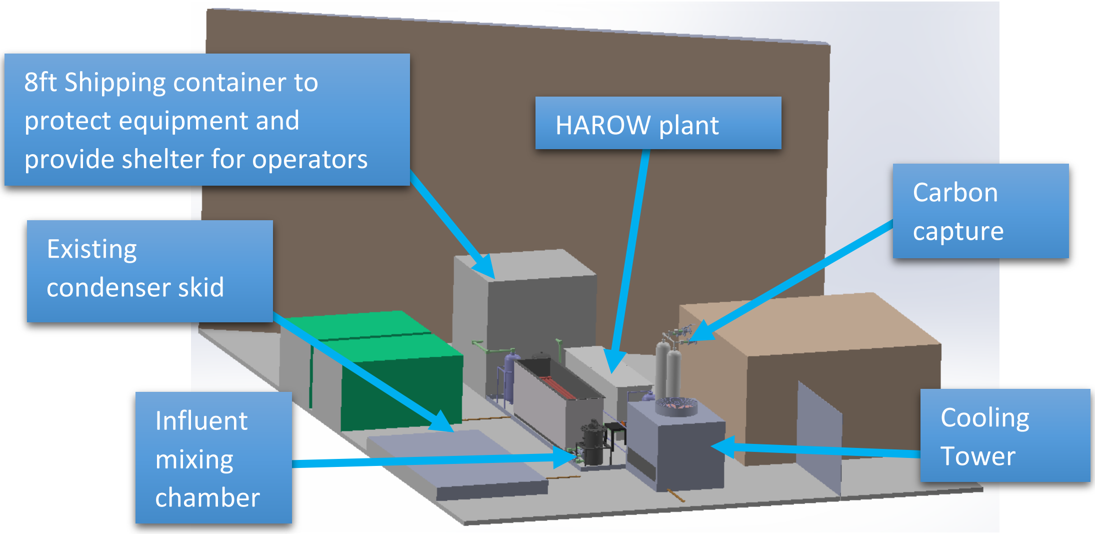


Figure 4 – Potential site showing the positioning of the HAROW plant, with other existing equipment.

5 Detailed approach to testing the innovation during Demonstration

A detailed testing regime has been developed based on assessing the performance of the technology on its ability to reduce the cost of hydrogen production by:

- Maximising biogenic CO_2 content: the two feedstocks being considered are effluent streams from bioenergy production processes i.e., crude glycerol from biodiesel production and digestate from anaerobic digestion. This will be demonstrated by showing the reduction in organic load of the aqueous streams used as feed for the process and CO_2 capture to enable negative carbon emissions.

- Reducing the costs of input fuels: energy integration will be carried out e.g., by matching the heating and cooling cycles within the plant. The possibility of using unrecoverable combustible gases produced from side reactions, to support the energy budget of the process will also be explored. The plant itself will maximize the energy contents of the feedstocks (crude glycerol and digestate) to displace the current fuel requirements for running biodiesel and AD plants, respectively.

The testing would consist of short functional tests, and a 1000-hour performance/ reliability test.

- Functional testing: Functional testing will involve steady operation for 8 hours and will evaluate the technology's viability and efficiency. At least 4 functional tests will be performed. However, additional tests will be performed if required to optimise performance. These tests will also assess the feedstock characteristics' impact on performance (e.g., crude glycerol-to-water ratio), product characteristics and quality (i.e., gas compositions), emissions and waste outputs (e.g., composition of effluent water). Functional testing will be conducted before and after the long duration performance testing to also determine any deterioration in process or equipment performance over the performance period.

- Performance testing: the long-duration, continuous performance testing will be conducted over a period of at least 1000 hours (probably running 3 shifts/day for 24-hour operation). This will provide assurance for viability of commercial operation, cumulative impacts of long-term operation, reliability, maintainability, plant cycling and scale up challenges.

Multiple sample points have been added to the P&ID (A to H) these will allow sampling of gas and water. During a functional test it is expected that around 6 samples will be taken at each point, and at least 1 sample at each point will be taken pre-shift. Samples will be sent to partner laboratories for analysis, but this will be supplemented by onsite gas/water analysis. As the testing progresses this may reduce the need for taking samples for off-site analysis.

Using a combination of sensors and the observations on the log sheet the environmental and energy performance of the system will be evaluated throughout the evaluation and performance testing. This will include updating the carbon life cycle assessment performed during the HAROW project.

6 Detailed Project Plan

A detailed project plan has been prepared considering the detailed engineering of the plant, construction and testing. Additional partners are expected to join the project.

The project plan is supported by a risk register. At this point, the Major Risks are seen, as follows:

#1 Operating efficiency is lower than predicted. Given that this is a new process, this is a possibility, and while the Lab trials carried out so far have shown efficiency is better than predicted, this may change at larger scale. The lab trials however give confidence that the technology will perform well enough for the demonstrator to work, but some over capacity will be designed in to allow for this.

#**4 Major equipment failure due to pressure**. Within the process, equipment has to operate at temperature and pressure, and will be built from standard high-pressure components. Equipment will be designed to well-established engineering principles, with additional safety factors added in. Safety reviews will be built into project planning.

7 Commercialisation Plan (informed by Phase 1)

An initial TechnoMarket Report was produced looking at aspects of the potential commercialisation of the HAROW process.

The main findings of this report can be summarised:

- The hydrogen market is big and growing – market pull will not be an issue for the right technology at the right price. Most of the energy industry and suppliers to the industry have an interest in hydrogen technology.
- Electrolysis is seen as the only true green hydrogen production method. However, it is at best 80% efficient, requires an abundance of renewable electricity and a plentiful supply of clean water.
- Other technologies for hydrogen are developing, but not at a significant commercial level.
- HAROW could have significant advantages in the hydrogen market, but there may be significant technical and cost issues that limit this.
- Feedstock for HAROW is readily available and depending on costs this may drive the market.

A commercialisation plan has then been developed, based on the technomarket study, conversations with possible stakeholders and the results of this project. Some significant points are:

- An initial analysis of possible waste feedstocks gives the total energy potential of HAROW as >1,000 TWh globally. This benefit is magnified by the cleaner water production capability of the process.
- Comparison with competitive technology is generally favourable, with the exception of the need for carbon capture, which electrolysis avoids (Figure 5)
- Possible use scenarios have been examined with the two extremes being presented in Figure 6.

Property	Electrolysis	Dark fermentation	HAROW	Explanation
Low carbon H_2	✓	✓	✓	
Works on contaminated water	✗	✓	✓	Electrolysis requires lots of clean water
Low energy requirement	✗	✓	✓	Electrolysis requires significant renewable energy to be green
No CO_2 storage	✓	✗	✗	
>90% conversion	✗	✗	✓	Electrolysis is typically 40-50% efficient, while 80% may be achieved in the future. Dark fermentation typically results in low conversions.
Clean water output		✗	✓	Low conversion in dark fermentation leaves contaminated water

Figure 5 – Competition matrix for HAROW vs electrolysis and dark fermentation. Electrolysis is selected as the current leading technology and dark fermentation as it utilises contaminated water in a similar way to HAROW.

The commercialisation of the technology has been discussed between the partners and is most likely to be done through a joint venture (NewCo), with the aim of NewCo having a package of intellectual property (IP) to licence to established operators in the market.

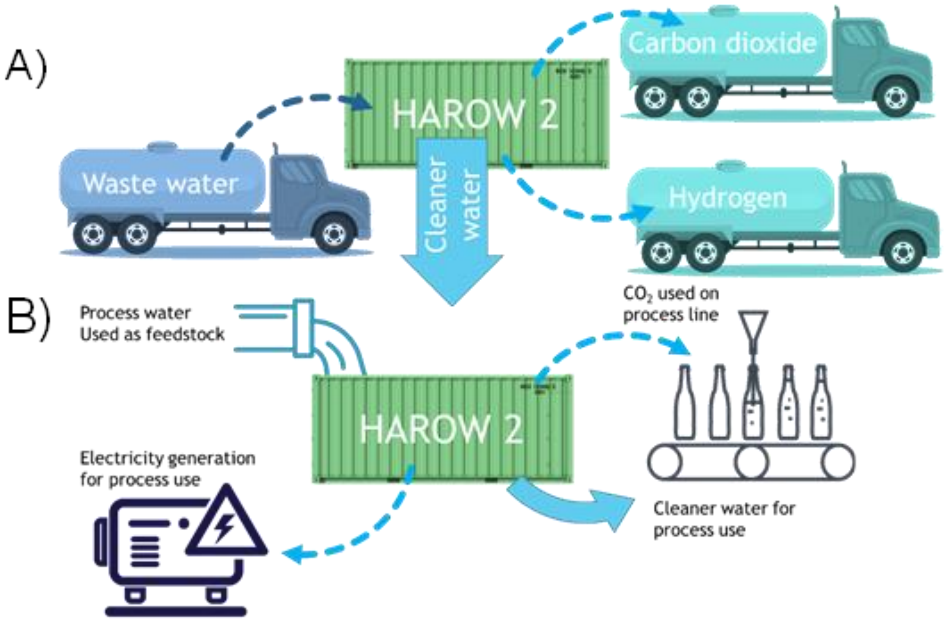


Figure 6 – Possible business models for HAROW showing two extreme scenarios A) HAROW unit located away from source of wastewater, away from demand for hydrogen and storage/use of CO_2. This is probably only viable at very large scale. B) HAROW unit located at source of wastewater and use point of hydrogen and CO_2. This will be viable at smaller scale

A business model for the operation of HAROW units has been developed which allows the viability of HAROW units to be assessed at different scales and hydrogen prices.

Sales forecasts have been prepared based on the addressable market for HAROW. The majority of income is assumed to come from licencing deals rather than direct sales and the majority of these are assumed to be outside the UK.

8 Summary and Conclusions

A study has been carried out based on Aston University's work on aqueous phase forming of organically contaminated wastewater.

The major technical outputs of this work have been:

- Demonstration that the proposed process works in continuous flow, improving on the batch processing previously done at Aston University.
- Conversion of the organic content of the water is between 80 and 90%.
- Concentrations of hydrogen ~40% (volume %) have been achieved with the potential to exceed >70% with some process refinement.
- The kinetics are between 5-10x faster than anticipated.
- A carbon life cycle assessment has shown that net CO_2 emissions from the process equals -2.15 kgCO_2e per kg of H_2 produced.

A project plan has been prepared for a follow-on project, including:

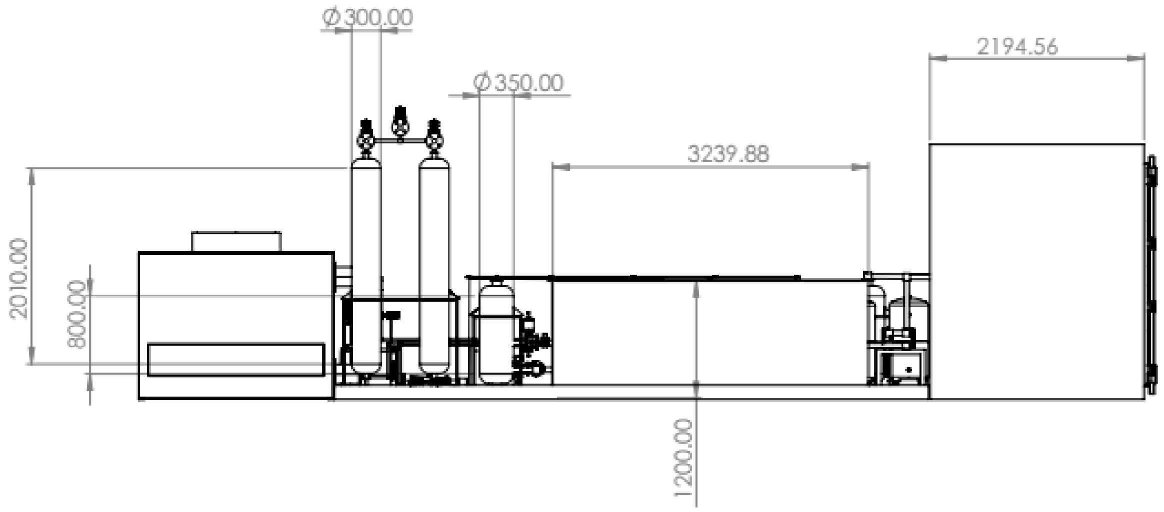
- Concept and basic engineering design for a demonstrator capable of producing 15T/year of hydrogen, with the major components fitting into the footprint of a 20 ft container.
- A supporting test programme and project plan will ensure that the project can be delivered in 2 years, with the required data generated and analysed.

A commercialisation plan has been prepared detailing:

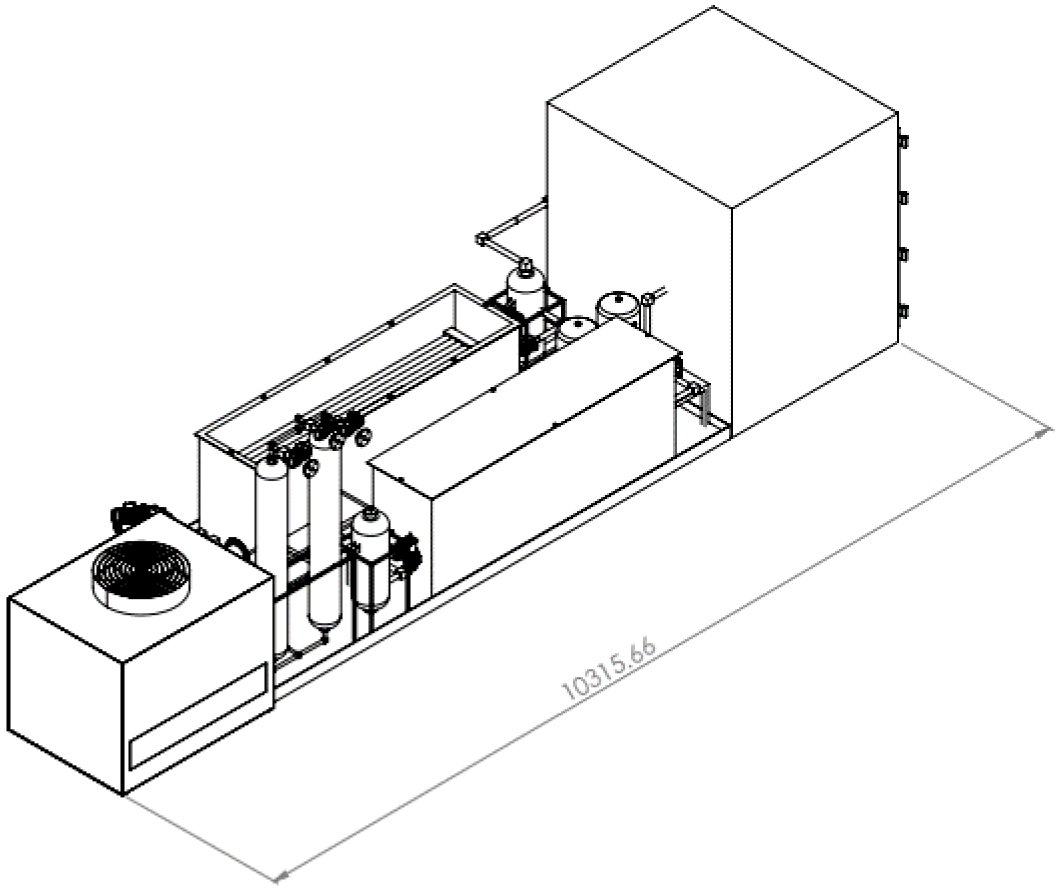
- An extensive market and the availability of waste feedstocks capable of providing 1% of the world's energy needs.
- A business model of how the process can be sold, largely by licencing to established operators. Sales forecasts based on the model.
- Modelling to show the viability at reasonable scale and hydrogen sales prices of £2-3/kg hydrogen.
- A plan to do this through a joint venture has been prepared by the partners.

Overall, a process has been demonstrated to produce hydrogen, that is scalable and has a clear route to market. There are no significant gaps in data that would limit scaling the process. Building a demonstrator is the next logical step based on these strong foundations.

Appendix A. Additional images of engineering model and drawings



Overview engineering drawing for the HAROW plant showing the major dimensions – side view



Overview engineering drawing for the HAROW plant showing the major dimensions – orthogonal view

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References

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