Australia's National
Science Agency

CSIRO Solar Thermochemical Hydrogen R&D Project

Mid project

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ARENA

CSIRO Energy

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1 Summary / Reflection at mid-point of the Activity

1.1 Project summary and scope

Thermochemical hydrogen production offers a low cost, thermal pathway for the production of hydrogen via a two-step processes that splits water into Hydrogen and Oxygen. The project has three programs that cover different aspects of the technology, demonstration of the complete water splitting process under a new solar thermal beam down concept, development of new catalyst materials to improve performance and a technoeconomic feasibility study of a methanol pathway for export of hydrogen.

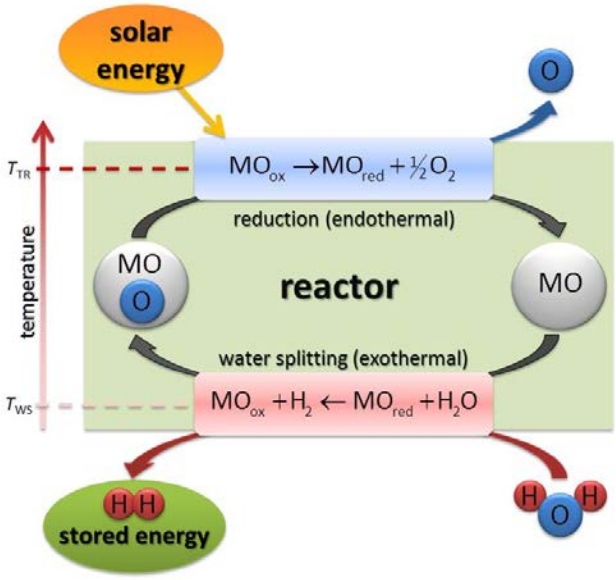

Figure 1 Simple diagram of the two-step water splitting process

The project is structured into 3 programs covering three distinct packages of work

- Program 1 – Solar thermochemical hydrogen (CSIRO)
  - Modification of CSIRO Solar field 1 to a beam down facility
  - Reactor development → Fluidised bed, Led by Niigata University (NU)
  - Experimental program
- Program 2 – NextGen Materials (CSIRO)
  - Targeting Perovskites structures
  - Computational Chemistry and machine learning (CSIRO D61)
  - Lab based experimental setup to confirm predictions
- Program 3 – Techno economics of methanol supply chain (IAE)

– Process design of TCH2 to Methanol

– Feasibility of methanol as hydrogen vector

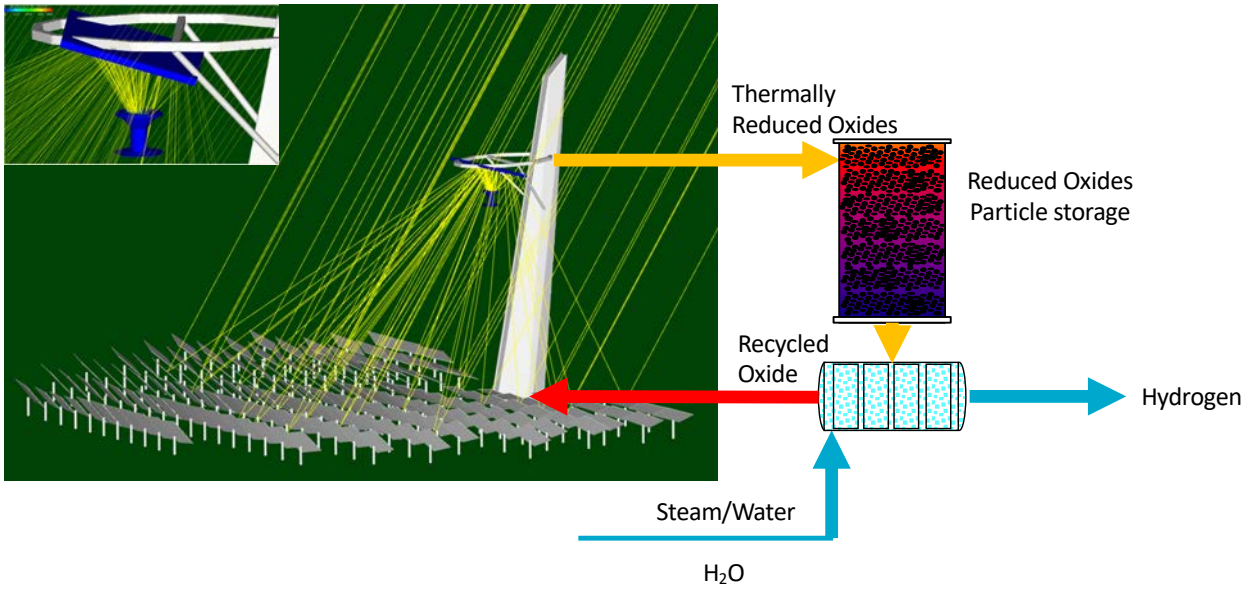

Figure 2 The overall demonstration system to be developed at CSIRO Newcastle for thermochemical water splitting for hydrogen production.

1.2 Program 1 – Demonstration facility

This program will demonstrate a working process for the two-step water splitting process. The work program has two parallel streams of activity with work in Newcastle focused on development on converting solar tower 1 to a beam down configuration and preparation of the field for hydrogen experiments while design of the fluidised bed reactor in being led by the University of Niigata.

Work at the CSIRO has focused on design of an optical system to deliver the required 1.6 MWt @ 1300 ^{o}C energy peak to the reactor. A number of configurations have been analysed with a final design favouring the flat reflector shown in figure 2 (RHS).

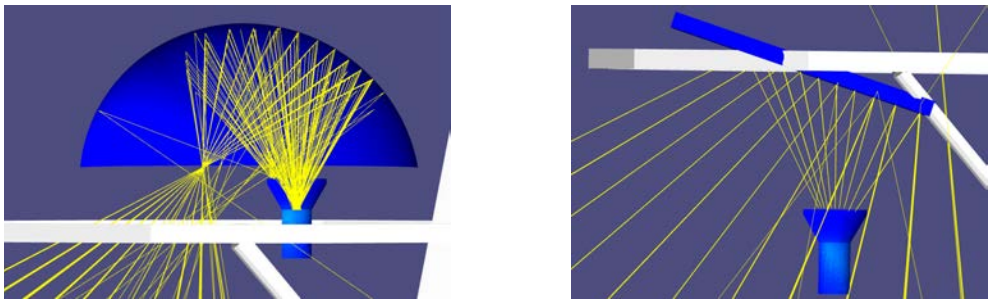

Figure 3 Ray trace results from field simulations

Niigata have completed the preliminary design of the fluidised bed reactor (Figure 4) and specification of the first catalysts that will be required to commission the equipment.

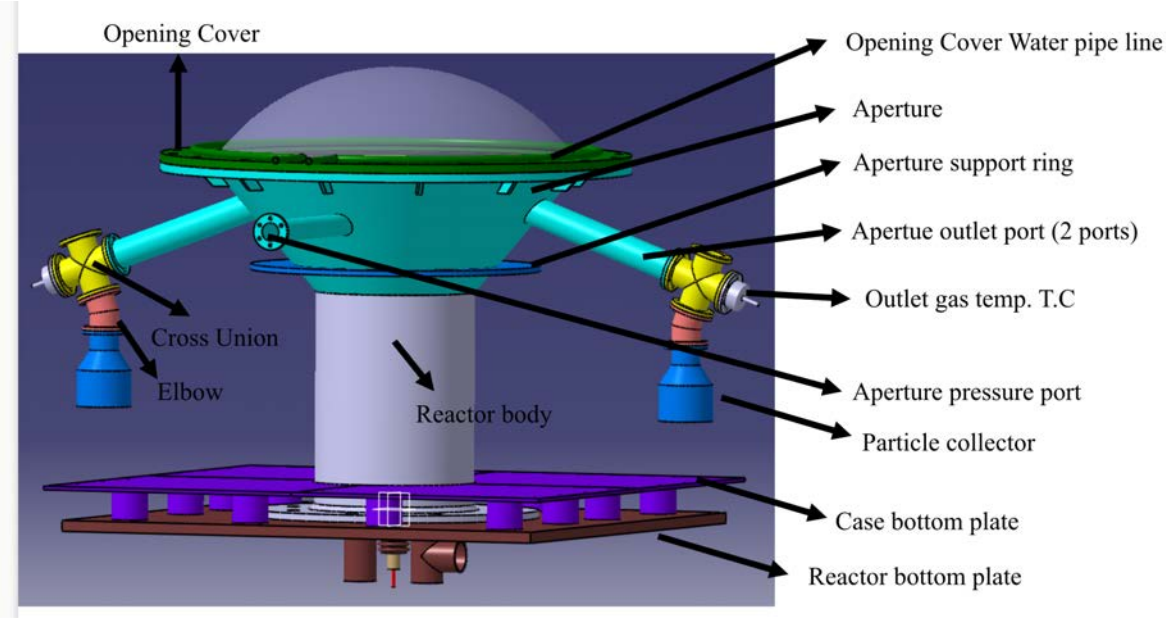

Figure 4 Niigata Fluidised bed reactor

1.2.1 Initial Concept

CSIRO Completed an initial concept sketch of the tower layout based on the optical model developed previously.

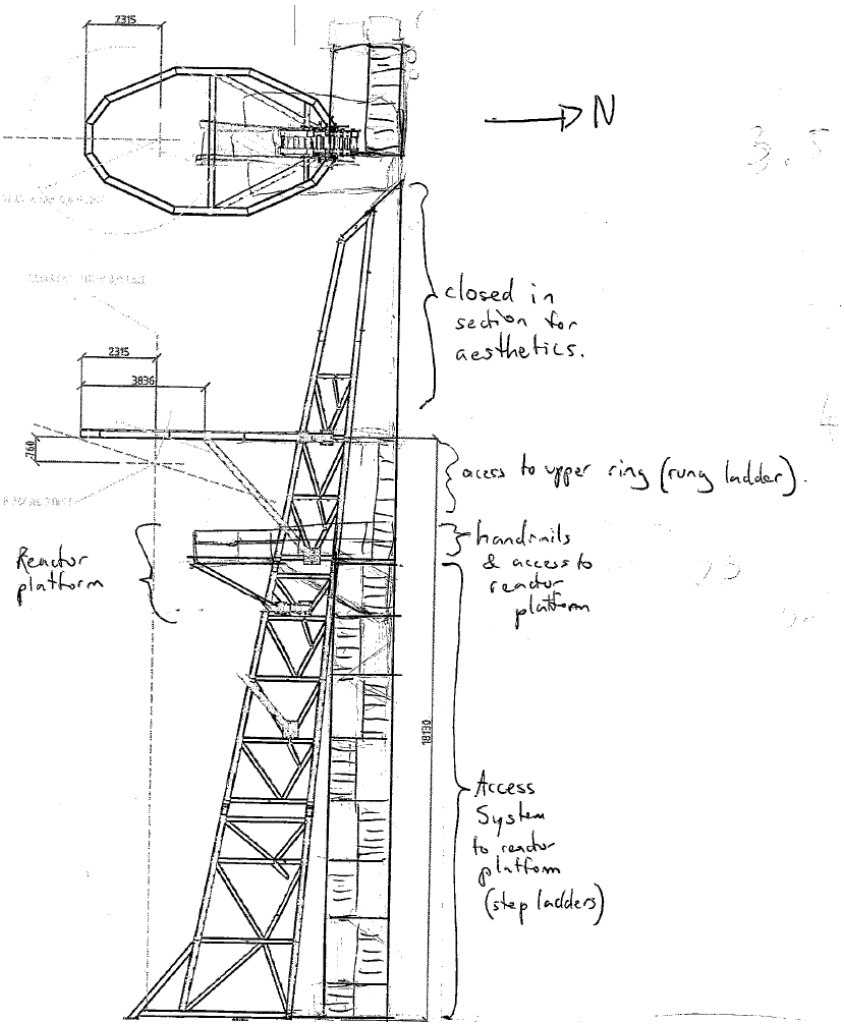

Figure 5 Initial Concept Sketch of Beam Down System

1.2.2 Overall Structural Conceptual Design

External Engineering Consultants Lindsay Dynan were engaged to complete conceptual designs for the stair tower to allow access existing solar tower. Lindsay Dynan were responsible for the original engineering on CSIRO Solar Tower 1. The design concept is shown in Figure 6.

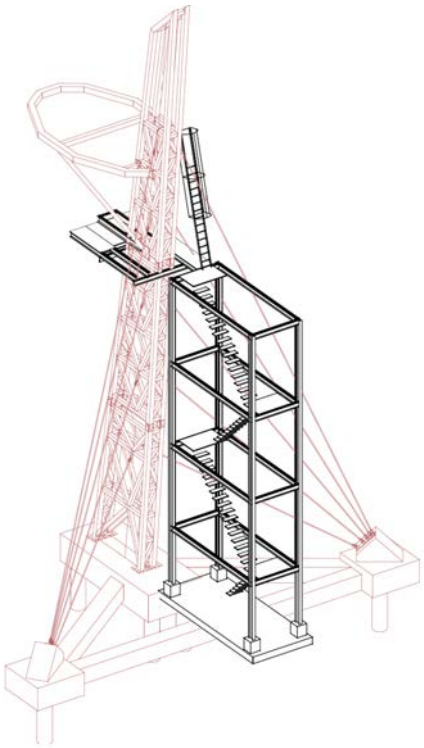

Figure 6 Concept for Stair Tower and Ladder for Access to the Reflector and Reactor Platform.

1.2.2.1 Detailed Reflector Support Structure Design

In conjunction with the optical modelling, CSIRO was able to complete a detailed design of the reflector and tower modifications. The monolithic reflector modelled in the initial stages of the project was discretised into 395x395mm panels, which were then culled to match the incoming irradiance from the heliostat field (Figure 7).

It was then clear that the original ring would need to be heavily modified to incorporate the reflector. A 'bulkhead' design was developed to change the ring to allow a simple and flexible interface to the tower (Figure 8).

The reactor platform design was developed as a set of rails that could carry the reactor in the north-south direction. This would be then surrounded by hand-railing when the reactor is close to the tower for maintenance. The aim is for the reactor to be lifted up and out within the remaining ring section by a crane without having to remove the reflector.

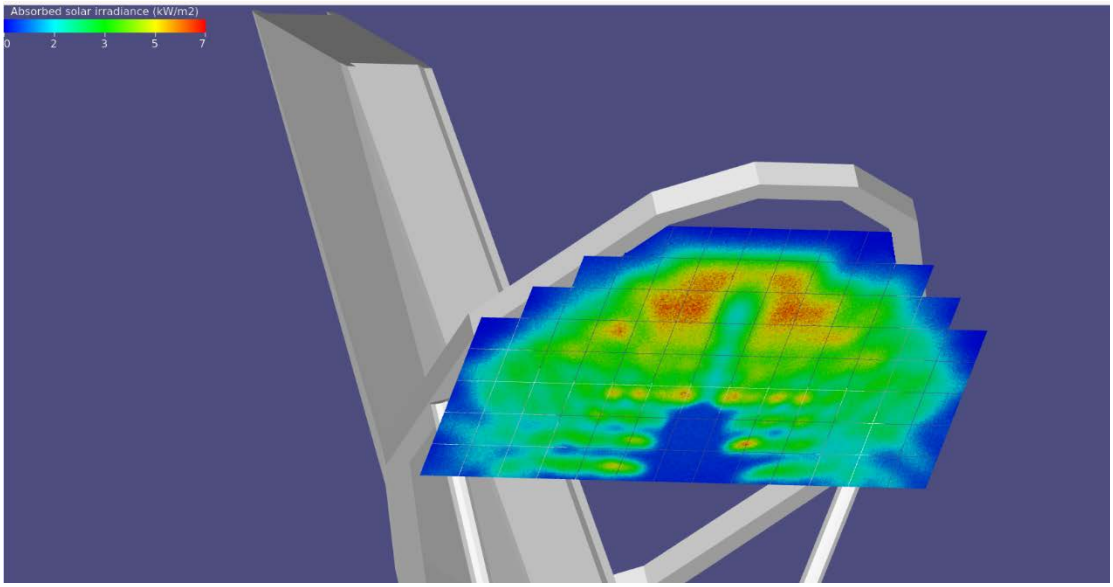

Figure 7 Irradiance map on Discretised Mirror Panels to form the Secondary Reflector

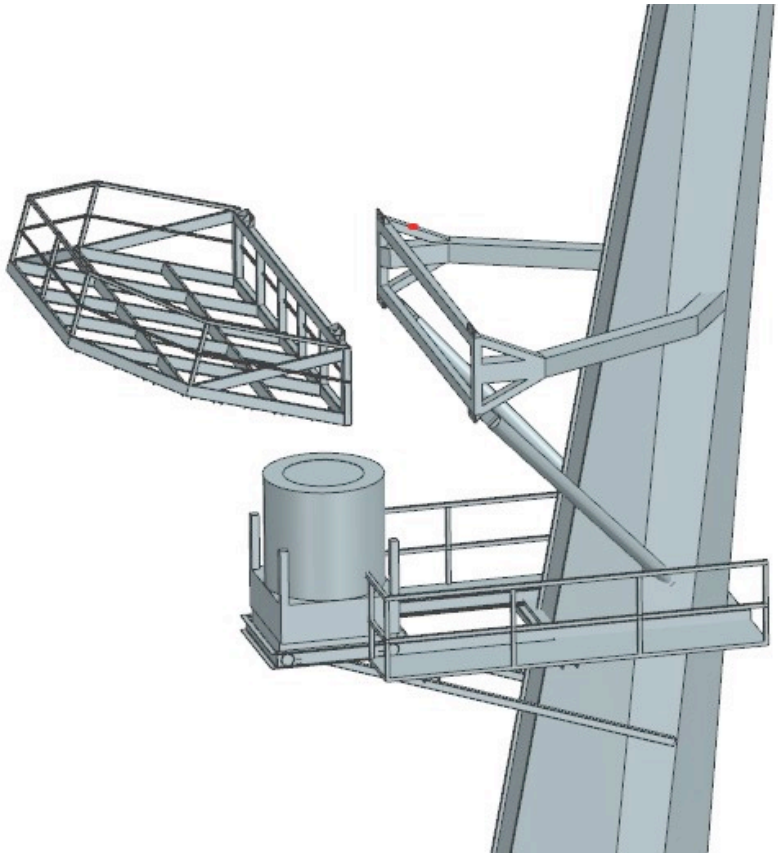

Figure 8 Bulkhead Design Concept

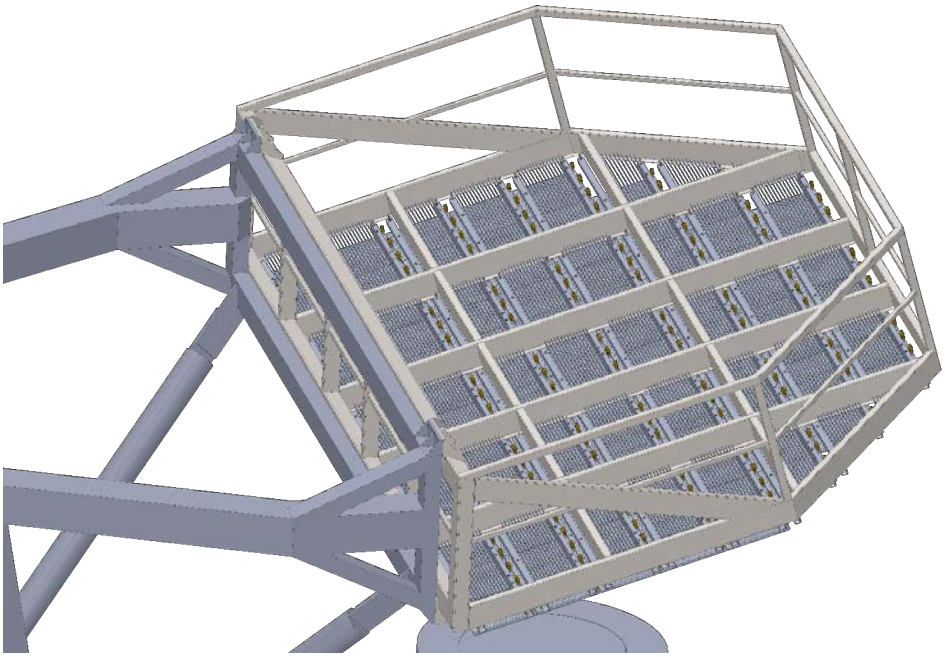

Figure 9 Detailed Design of Reflector Support System

1.2.3 Detailed Structural Engineering

Lindsay Dynan have now completed structural analysis on the tower due to the amended support arrangement provided. This includes the amended ring member, struts, connections back to the tower and the global strength/stability of the tower itself.

Loading conditions include:

- Self-weight
- Equipment weights
- Wind loads
- Earthquake loads
- Maintenance traffic loads

1.2.4 Construction Commencement

Extensive surveys of the existing ring have been completed. The ring has been now been removed from the tower and transported to a local manufacturer ready for modification.

Figure 10 Ring Removed from Tower in October

1.2.5 Solar Field 1 Refurbishment

The actuators on the Heliostats in Solar Field 1 have been replaced in September 2020. This ensures the heliostats will be running improved hardware and the most recent version of CSIRO's heliostat control software.

1.3 Program 2: NextGen Redox Materials Development

The main objective of this program is to discover a novel set of perovskites performing solar thermochemical water splitting more efficiently than current state-of-art CeO_2. This work is assisted by the creation of a novel machine-learning algorithm (Redox-Machine) for screening thousands of perovskites metal oxides targeting the highest hydrogen production capability. This task is combined with an experimental demonstration of the perovskites in lab and reactor scale. Dr. Fischer (Postdoctoral Fellow) and Mr. Perry (PhD candidate) have been recruited during this current milestone for the machine-learning code development and experimental demonstration tasks respectively. Currently, a perovskite database is under development collecting all available data from different material repositories e.g. "The Materials Project" database (Figure 1.a). The perovskite database contains currently more than 2900 materials and their crystallographic data. The experimental task has been started with currently 8 materials fully synthesized and analysed

by XRD[1], SEM[2] and TGA[3], including CeO_2 as our baseline material. A collaboration with Arizona State University has started and Dr. Bayon (program leader) will perform XPS experiments.

A database has been established from the "The Materials Project" repository (MP). This database has 2105 entries of perovskites. For each of these entries, we have established 1133 features which are input for the machine learning algorithm. A feature is an individual property e.g., atomic weight or boiling point. It can be also a function of multiple features e.g., mean atomic radius or maximum atomic number of a composite.

Most of our features are not depended on quantum chemical calculations or experiments (964 features) hence they are usable for novel perovskite structures. We also developed structural features for the entries with optimised unit cells (170 features).

Further, the possible set of perovskite formulas was created. The metal doping ratios were selected on the computational cell size of $A_8B_8O_{24}$, with possible doping on A-site (A') and B site (B'). These formulas were created with a generalised chemical form of $A_xA'_{(1-x)}B_yB'_{(1-y)}O_3$ with x, y = {0, 0.125, 0.25, 0. 375, 0.5, 0.625, 0.77, 0.875, 1}. A and B are metals and our selections are shown in Table 1. The elements were chosen, as they are non-toxic, non-radioactive and inexpensive. In the MP repository also structures with other metals are used to train the machine learning models.

Table 1 Possible elements for perovskite A and B-sites.

A-site elements	Ba, Bi, Ca, Ce, Dy, Gd, La, Mg, Pr, Sm, Sr, Y, Zr
B-site elements	Al, Bi, Co, Cu, Fe, Ga, Mg, Mn, Mo, Nb, Ni, Se, Sn, Ti, W, Zn, Zr

A-site elements are larger than B-site elements. Some elements (e.g. Zr and Bi) could dope either a A- or B-site. The Shannon radii was used as an ionic radius with either 8 or 12 oxygen atom coordination.[2] For some oxidation states, these values were not available. These were linearly predicted with the method of Kudoh et. al. This way all structures are assumed to have perfect coordination.

From the elemental selection, there are 1 million formulas possible. These were further reduced to 200 000 which are predicted to crystallise in perovskite structure. This was determined by the new tolerance factor ($0 < \tau < 4.18$). the tolerance factor[4].

[1] X-ray diffraction (XRD)

[2] scanning electron microscope (SEM)

[3] thermal gravimetric analysis (TGA)

[4] The tolerance factor tolerance factor, is used to predict the stability of the perovskite structure based only on the chemical formula, ABX3, and the ionic radii, ri, of each ion (A, B, X)

Further, we developed an algorithm which creates doped perovskites unit cell structures. These structures are created depending on the materials database lowest-energy perovskite structures which are closed to the new element atomic radii. This algorithm gives us the input structure for multiple unit cells (e.g. cubic or orthorhombic) which can be used for Density Functional Theory (DFT) calculations

1.3.1 Machine learning

The atomic features were used to predict the formation energy and the certainty of the prediction with Random Forest (see Appendix for more information). Firstly, for the values from our database. Secondly, to predict it for our 200 000 possible perovskites. The formation energy is an important value for the stability of materials. Materials with a low absolute value of formation energy are less likely to withstand the high temperatures of the solar thermal process.

The certainty of the prediction was implemented with confidence intervals. They should give us the structures which are least well predicted with the current dataset. To improve our methods the least confident predictions are the values which will be calculated with DFT and the step of prediction formation energy with a larger dataset can then be repeated.

In another step, we also used a semi-supervised algorithm called label propagation to predict if a material produces hydrogen or not. For the labels, we used a literature search on perovskite oxides which produce or not produce hydrogen. In Figure 11, all the predicted labels are visualised with t-distributed stochastic neighbour embedding (t-SNE). In the image only structures of the possible perovskites with a high absolute value of formation energy (< -3.7 eV) are shown and marked as '*me*'. There are 81 materials formulas which have a low formation energy and are predicted to produce hydrogen.

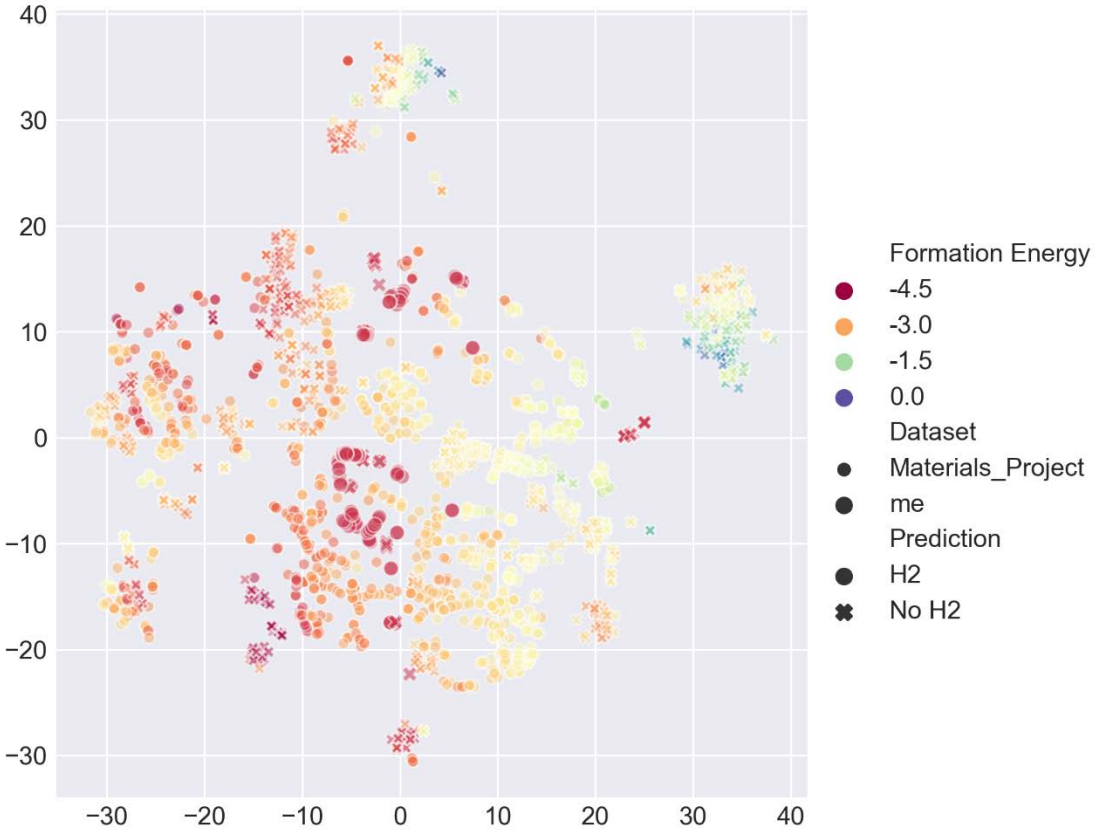

Figure 11: Label propagation of materials which produce hydrogen. The colour is from a spectrum of formation energy per atom in eV and the size of markers is from the origin of the data. The visualisation is with t-SNE and the axes are without physical meaning.

1.4 Program 3 – Technology Technoeconomics

Program 3 captures the technoeconomic of the process and applies it to a methanol based transport cycle to enable utilisation in Japan. This part of the project is led by the Japanese Institute of Applied Energy[5] an autonomous, non-profit organization conducting technology related research in broad energy areas. The IAE's researchers conduct studies and organize projects with the broad network developed among industry, academia and the government.

The proposed hydrogen transport loop is presented in Figure 12, and demonstrates the usage of methanol as the carrier. Utilising methanol as the carrier has many advantages

- Methanol is liquid allowing existing shipping infrastructure to be utilised
- Methanol has an existing market as a commodity and therefore its handling and safety characteristics are well understood

[5] https://www.iae.or.jp/e/about-us/

- The calorific value of methanol is similar to existing fuels and therefore can be used as a direct displacement to existing fuels in the short term, enabling rapid market development for hydrogen
- Carbon dioxide acts as carrier and is not released rather recycled back to the start of the process.

Process and cost models have been completed for the complete cycle which enabled the cost of production of methanol, this included:-

- cost for each process of hydrogen production and its storage,
- methanol synthesis and its storage,
- transportation of methanol.

The methanol production cost was then analysed with sensitivity calculations for 4 cases using the equipment costs of hydrogen production and CO_2 procurement and transaction prices as parameters.

In all cases, the production cost of methanol was in the range of 300 to 600AUD/ton MetOH. In context the market price of methanol is about 300AUD/ton MetOH, allowing some confidence that the cost range is sufficient to withstand market competition and with improvements in future technology and establishment of mass production system.

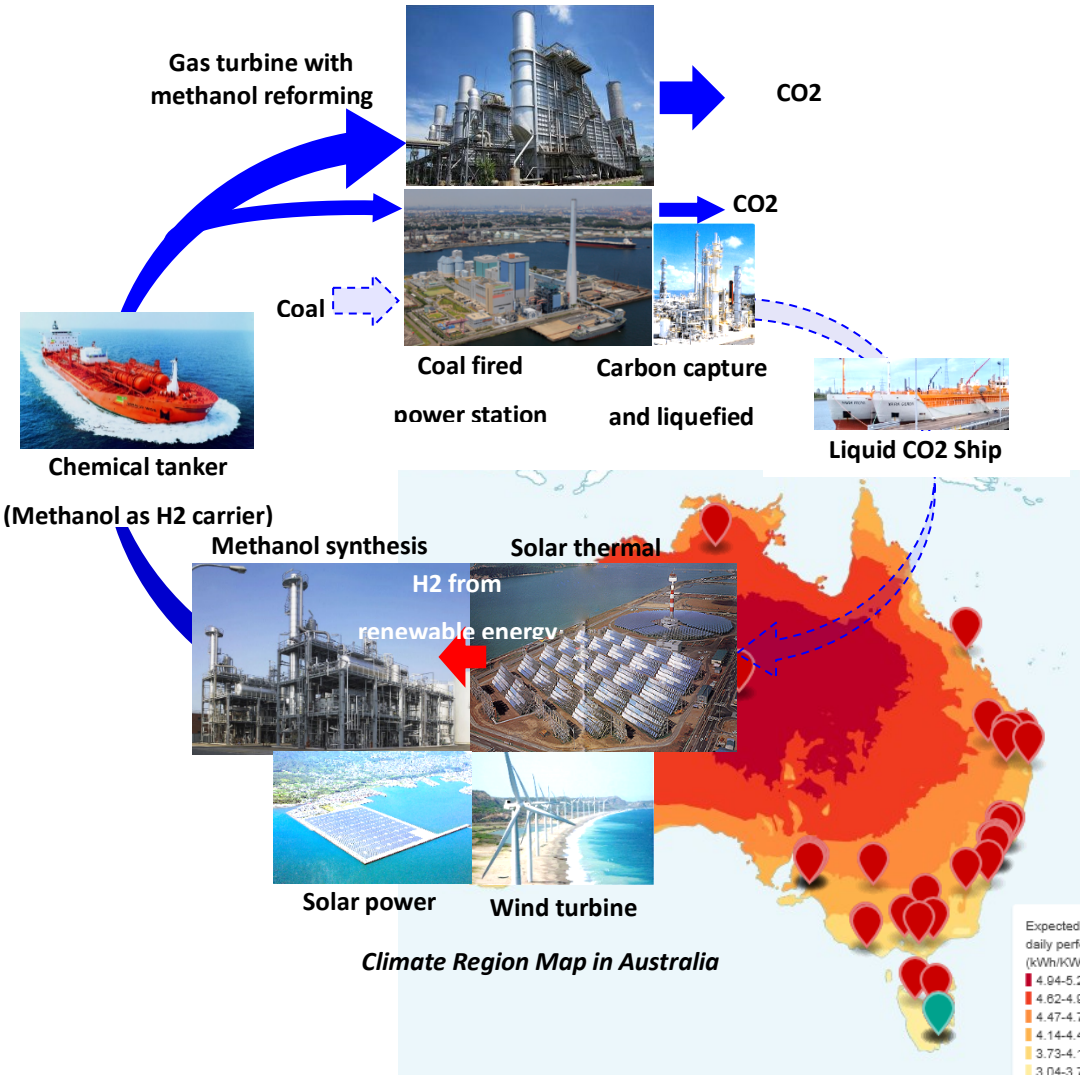

Figure 12 **Proposed cycle of methanol transport for Hydorgen**

In 2021, the cost estimation will be reviewed in light of the experimental data from the beam down system underway by CSIRO and Niigata University. This allows an assessment of how much the hydrogen produced by this project is different from the current and future hydrogen market cost. Similar verification will be carried out with respect to the target cost of hydrogen in the technological strategy of Australia and Japan.

Additionally, a technical assessment will consider technical issues of this technology path and it potential to reduce the hydrogen cost.

2 Key highlights and difficulties experienced

2.1.1 Highlights

- CSIRO 200 kWt beam down facility is under construction and expected to be operational by March 2021. The facility will enable solar energy of 200kWt to be directed to a horizontal surface at peak energy inputs of 1600 kWt/m2 and operating temperatures up to 1500 oC.
- CSIRO's solar thermal beam down optical system has generated considerable interest for other applications which are requesting access to the system. This includes Australian technology start up – MGA thermal and CSIRO Mission Net Zero – for mining applications. In addition, Australian and international universities have requested information on the system and its capabilities
- Negotiations are continuing with Nippon Kayaku Corporation as a commercialisation partner for the technology.
- Laboratory work has identified suitable perovskite materials that have potential to outperform the current best Ceria material.

2.2 Schedule and Impact of COVID

- Program 1 has been impacted in 2020 initially due to china closing down and delays in parts, shipping delays at the Australian ports and CSIRO dictated closures of sites to external contractors.
- Program 2 is lab/office based through this part of the project and is unimpacted.
- Program 3 is office based through this part of the project and is unimpacted. However, delays in program 1 will flow through to this program towards the end of the project.

As a result, the project has requested and been approved a variation to accommodate delays in construction as a result of COVID19 and restriction of contractors on site.

The current project plan is shown below.

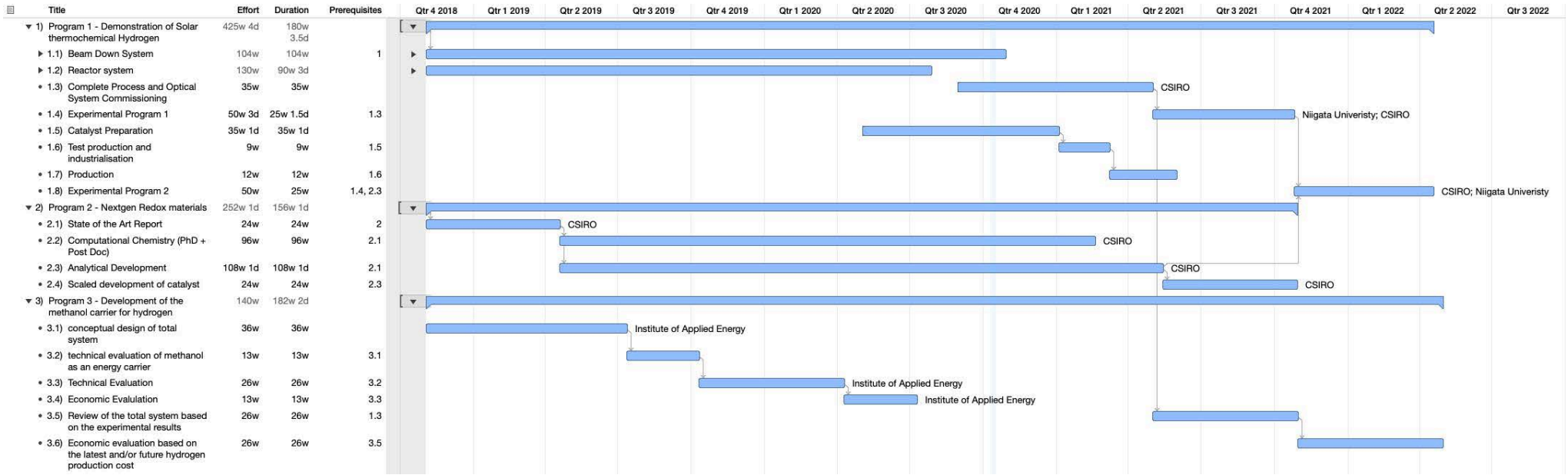

Figure 13 Current GANTT chart of project planning

3 Commercialisation prospects

The technology is still in the early days, with the completion of the Beam down facility critical to showcasing the potential of the technology.

There has been interest from a number of corporations from Japan to be included in the project.

- A Japanese Chemical corporation They are a catalyst supplier who have a desire to be a commercialisation partner for technology that the project will develop. I will meet again with the company in November to discuss their formal involvement.
- There is also continuing interest from Japanese energy corporations which are linked via the IAE.
- There are also a number of component suppliers looking for a formal involvement in the project such as Mitaka Kohki Co., Ltd. – Optical Equipment, Techno Quartz Inc – Quartz windows

The project is also collaborating with Arizona State University in the USA through Program 2, this work seeks to generate new methods of analysis of materials that has the potential to vastly improve the time required to screen materials. Summary of knowledge sharing activities completed (e.g. publications, conferences, patents)

4 SUMMARY OF KNOWLEDGE SHARING ACTIVITES COMPLETED

Knowledge sharing activities have been limited mostly due to the stage of the project, and progress towards completion of the beam down facility. The beam down facility is unique in the world and is expected to create significant interest worldwide once operational and performance verification has been completed.

4.1 Journal Publications

- Alicia Bayon, Alberto de la Calle, Krishna Kamol Ghose, Alister Page, Robbie McNaughton, Experimental, computational and thermodynamic studies in perovskites metal oxides for thermochemical fuel production: A review, International Journal of Hydrogen Energy, Volume 45, Issue 23, 2020, Pages 12653-12679, ISSN 0360-3199, https://doi.org/10.1016/j.ijhydene.2020.02.126

- Potter, Daniel; Hetherton, Lachlan; Thomas, David; McNaughton, Robbie; Watkins, Damien. An integrated optimisation functionality for Workspace. In: 23rd International Congress on Modelling and Simulation (MODSIM2019); 1-6 December 2019; Canberra.

- J. M. Fischer, M. Hunter, M. Hankel, D. J. Searles, A. J. Parker, A. S. Barnard, Accurate prediction of binding energies for two-dimensional catalytic materials using machine learning, ChemCatChem 2020, 12, 5109.

- S. Barnard, B. Motevalli, A. J. Parker, J. M. Fischer, C. A. Feigl and G. Opletal, Nanoinformatics, and the big challenges for the science of small things, Nanoscale, 2019,11, 19190-19201

4.2 Presentations:

- McNaughton, Potter, and Collins, “Development of the CSIRO 200kWt beam down facility” 2nd HiTemp Forum
- C3DIS 2019 - Feature engineering for catalysis, material in-between periodic and molecular systems
- Materials Oceania 2019 - Feature selection for machine learning of surface catalysts
- IUMRS-ICA 2019 (20th International Union of Materials Research Societies International Conference in Asia) - Machine learning feature engineering of molecules on materials

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