

The University of New South Wales

Waste Biomass to Renewable Hydrogen

MID-TERM ACTIVITY REPORT

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PROJECT SUMMARY & SCOPE

Summary

The Project is focussed on establishing a tandem biomass reforming system capable of extracting hydrogen from biomass with only solar energy inputs (Figure 1). Biomass is the second most abundant resource on Earth that is rich in hydrogen. Utilising biomass as a H₂ source in an electrolytic system has many advantages, from energy to economic perspectives. Biomass molecules, such as sugar- or fat-derived alcohols, can be produced at very low cost from raw biomass streams (e.g. sugars and vegetable oils in waste) and are more amenable to hydrogen extraction using an electrochemical system than the more traditional water electrolysis. H₂ extraction from biomass by electrochemical means is selective and scalable, it delivers zero CO₂ emissions and has the additional advantage of producing value-added carboxylic products which can potentially be used for plastics fabrication. The primary challenges associated with biomass electrolysis are: (1) poor catalyst H₂ extraction ability in the biomass electrolyser; (2) the need for pre-conditioning of the raw biomass to produce bio-alcohol derivatives as a feed-stock; and (3) a lack of system integration, performance optimization and tools for process upscale.

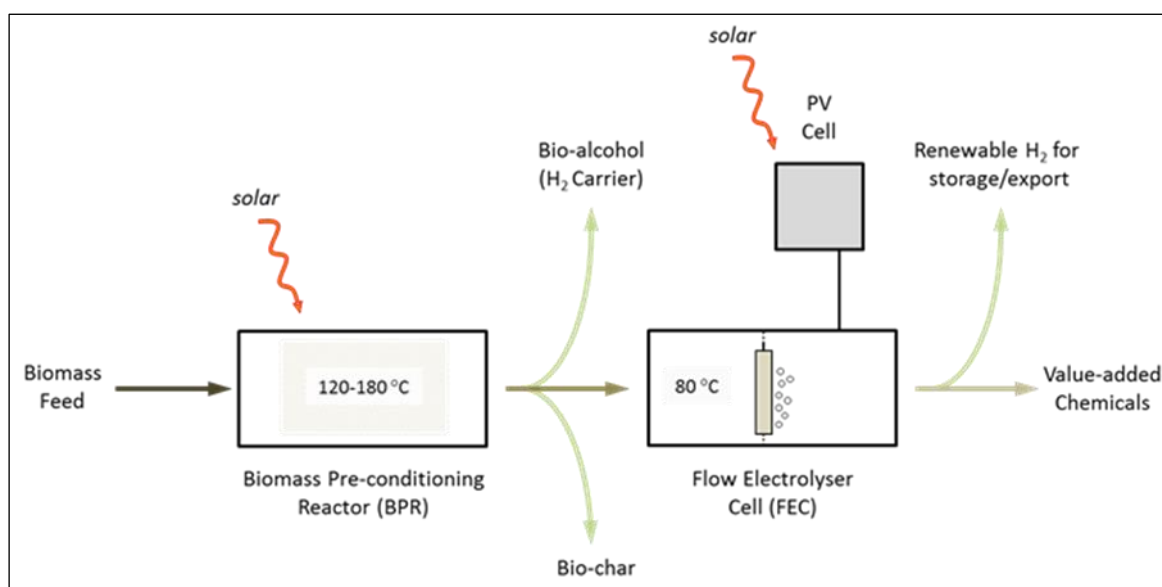


Figure 1: Process overview of biomass reforming system

Scope

The Project is designed to address these three challenges by developing three primary integrated aspects:

- 1) to deliver a (50 mL/min throughput) solar-collector biomass pre-treatment reactor (SC-BPR) for preconditioning the biomass for hydrogen extraction;
- 2) to provide a (0.5-1 L capacity) photovoltaic powered flow cell electrolyser (PV-FEC) for extracting the hydrogen from the preconditioned biomass;
- 3) to offer a computational model for predicting pilot-scale operational parameters for the BPR-FEC system.

Progress to Date

(1) *Solar Collector Biomass Pre-treatment Reactor (SC-BPR).* A 100 mL volumetric capacity laboratory-scale BPR array has been established and the working conditions have been defined. The conversion of sucrose, representing a control biomass, into 5-hydroxyfurfural (5-HMF) is the reaction used to assess BPR performance. 5-HMF is the targeted product as it represents the desired feed-stock for the ensuing FEC system.

(2) *Photovoltaic Powered Flow Cell Electrolyser (PV-FEC).* A 50 mL capacity FEC system has been established and shown to be capable of generating hydrogen from 5-HMF. The sensitivity of the FEC array to various operating parameters is currently on-going.

(3) *Computational modelling.* A model for the laboratory-scale BPR was successfully developed and validated using data taken from the BPR experiments and literature. A model for the laboratory-scale FEC was successfully developed, and is undergoing validation pending completion of the sensitivity analysis (experimental) to various operational parameters.

KEY HIGHLIGHTS AND DIFFCULTIES EXPERIENCED

Solar Collector Biomass Pre-treatment Reactor

A 100 mL laboratory-scale BPR (Figure 2a) was used to pre-condition the sucrose biomass (into 5-HMF and other products) in a sealed environment at a set temperature. Conversion of sucrose into 5-HMF can be visually observed by a colour change from clear to brown in the solution as shown in Figure 2b. Ideal operating conditions to give the best 5-HMF yield were found to be: temperature = 150°C, sulphuric acid concentration = 0.05 M. The laboratory-scale BPR was shown as capable of converting sucrose into 5-HMF at an ~17% yield (0.034 M) from 100 mL of 0.1 M sucrose solution (Figure 2c).

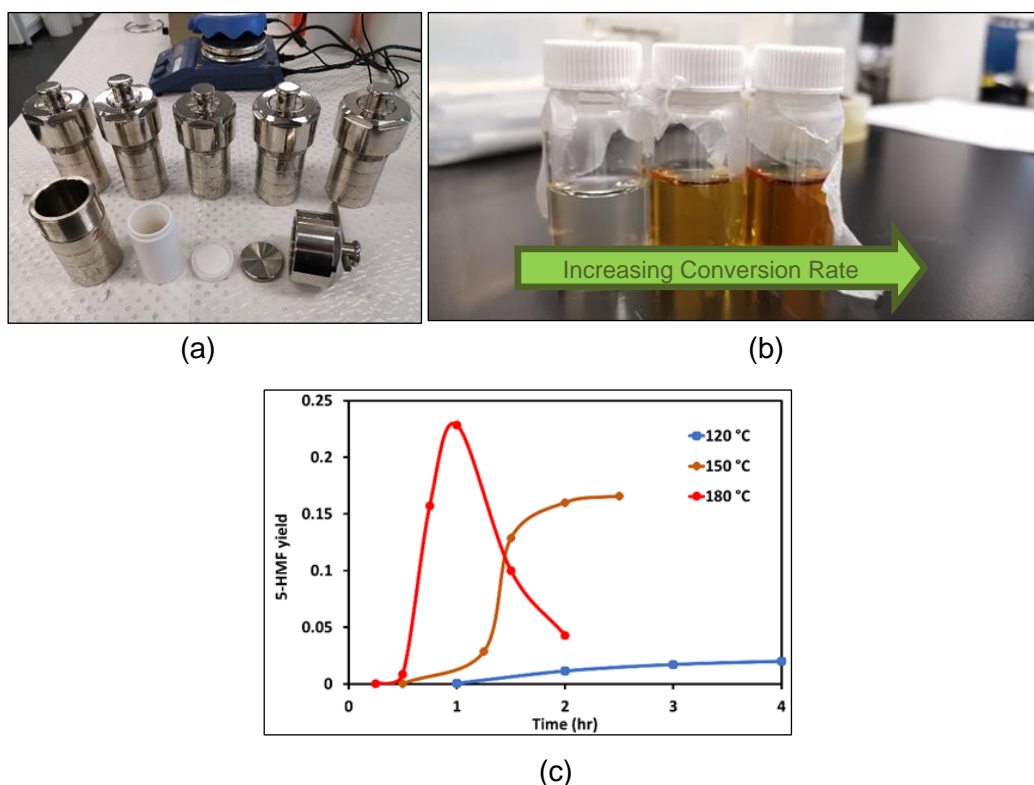


Figure 2: (a) Laboratory scale BPR reactors; (b) Conversion of sucrose with time to produce 5-HMF; (c) 5-HMF yield from sucrose with time at different BPR temperatures.

The development of a scaled-up SC-BPR for outdoor use is underway with a prototype unit comprising a concentrated parabolic collector (CPC) array with an evacuated solar tube (EST) reactor and adjustable reflective wing (see CAD drawing in Figure 3) being the current design of choice.

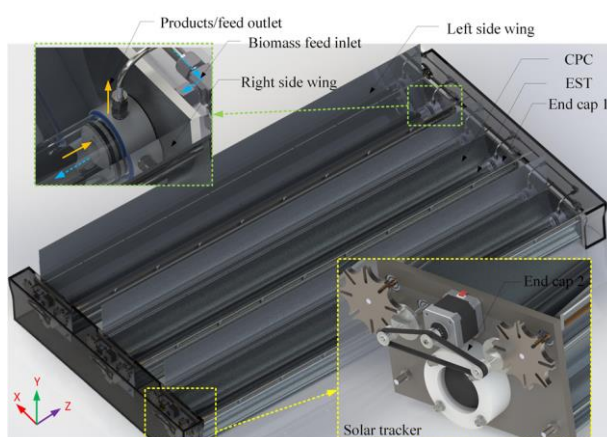


Figure 3: 3D-CAD (Computer-Aided Diagram) schematic of SC-BPR design with adjustable reflective wings.

Difficulty Experienced/Lesson Learned #1

Laboratory-scale BPR heating and cooling effects. Heat was provided to the laboratory scale BPR (Figure 2) using an oven. The BPR was placed in the oven once it had reached the desired reaction temperature. When removing the BPR from the oven, it required cooling before a sample could be taken. The BPR therefore takes time to heat and cool where it was realised the reaction will start at some time prior to the BPR reaching the reaction temperature and continue for some time following removal of the BPR from the oven. While the time taken for the BPR to reach the reaction temperature cannot be accelerated, the cooling time was shortened (and the reaction quenched) by placing the hot BPR in cold water upon removal from the oven. The implications of this, while not too significant for the small laboratory-scale BPR, will be more significant for the scaled-up BPR arising from the larger solution volume to be heated and the different heating system (solar collector). Integration of the heating/cooling effect of the reaction solution into the model of the scaled-up system will be necessary to effectively reflect biomass conversion.

Photovoltaic Powered Flow Cell Electrolyser

A laboratory scale PV-FEC (50 mL capacity) system was constructed and commissioned as shown in Figure 4a. The system comprises three key components: an electrolyser with a membrane electrode assembly (MEA) setup; a product collector and an electrolyte circulation system. The sensitivity of the FEC array to various operational parameters is currently under investigation. An electrocatalyst designed to accelerate the extraction of H₂ from the 5-HMF was developed, comprising cobalt hydroxide loaded on a nickel foam support (Figure 4b). The developed electrocatalyst was shown capable of generating ~26.6 mL of hydrogen from 50 mL of a 10 mM 5-HMF solution (Figure 4c).

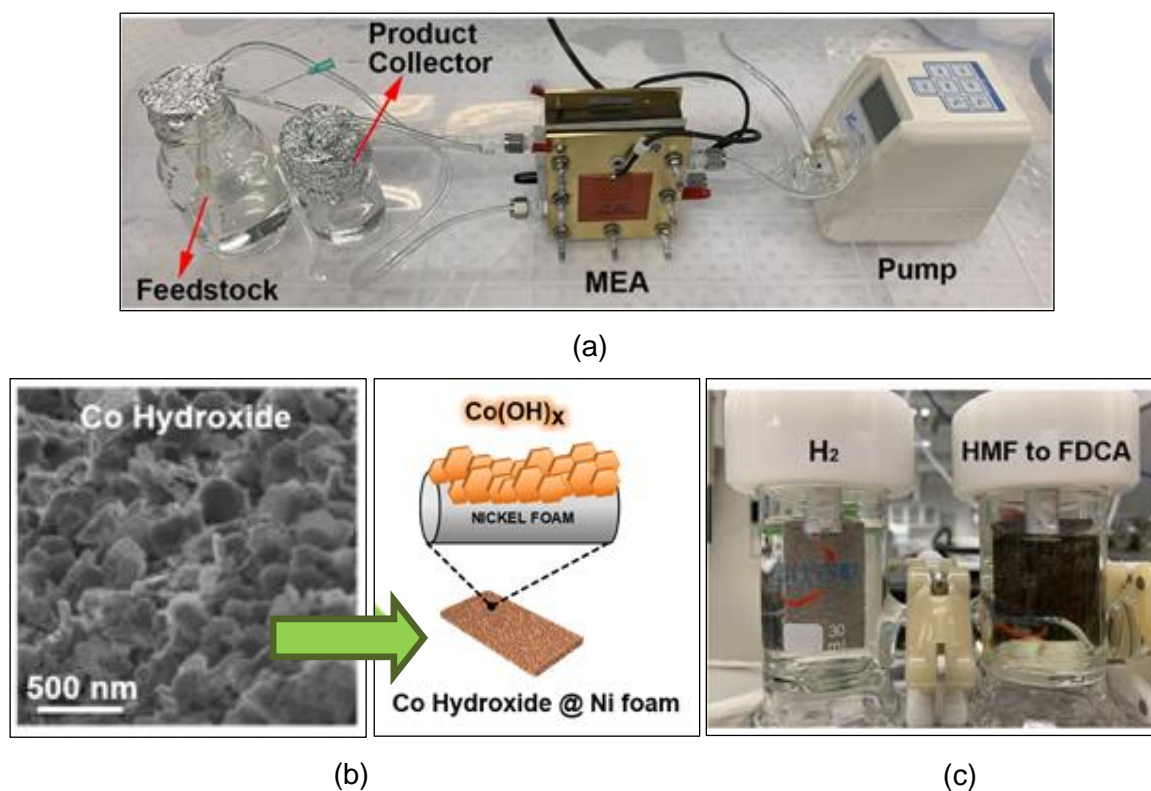


Figure 4: (a) Laboratory scale FEC system (50 mL capacity) comprising an electrolyser with a membrane electrode assembly (MEA), a product collector and an electrolyte circulating system; (b) Developed Co hydroxide electrocatalyst for use in FEC system; (c) Hydrogen generation (in left compartment) from 5-HMF electrolysis (right compartment) using the Co hydroxide electrocatalyst.

Difficulty Experienced/Lesson Learned #2

Disparity in pH operating conditions between SC-BPR and PV-FEC. Hydrogen extraction from 5-HMF within the FEC system currently functions well under an alkaline environment (pH > 7). Using sulphuric acid for biomass conditioning in the BPR means the effluent from the BPR system (which becomes the feed-stock for the FEC system) is currently acidic (pH < 7). Problems will likely arise regarding electrocatalyst stability (and diminished FEC performance) due to acidic nature of the BPR effluent. Measures to address this challenge are being examined by the CI team and include: (i) pH adjustment of the BPR effluent to make it alkaline. Having an intermediate pH adjustment stage imposes the

drawback of increased process costs; (ii) developing a FEC electrocatalyst which is resistant to acidic conditions; (iii) introducing an immobilised heterogeneous metal oxide catalyst in the BPR which can facilitate sucrose conversion into 5-HMF without the need for sulphuric acid. The advantage of options (ii) and (iii) is that no intermediate pH adjustment will be needed.

Computational Modelling

The computational component of the project is designed to understand and optimise the system and create innovative reactor designs. Designs and data from the team members will be tested and optimised to predict system performance, aid with the scaling up process and enhance system efficiency.

BPR model development and validation

A Computational Fluid Dynamics (CFD) model for describing the production of 5-HMF in the lab-scale BPR has been developed. It predicts the behaviour of the sucrose conversion reaction to form 5-HMF and other products. Model validation has also been completed. The model is able to be scaled up and adapted to the BPR prototype modelling in the next phase of the project. The model offers a cost-effective way to evaluate BPR design and performance under different operating conditions and structural configurations.

The result from the kinetic model designed to describe the changing concentration of intermediates/products generated during sucrose conversion with time in the laboratory scale BPR (to be integrated within the CFD model) is shown in Figure 5. The model simulates the conversion of sucrose into 5-HMF and other key products at a defined; (i) temperature (T), (ii) initial sucrose concentration (C_{suc}) and (iii) acid concentration (C_{acid}). It has been validated using experimental data (Figure 2c) and findings from the literature.

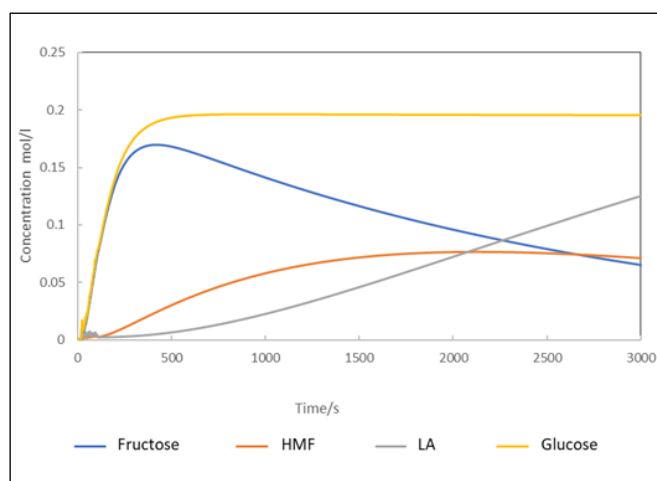


Figure 5: Simulation results describing the kinetics of product yield with time during sucrose conversion. Target product is 5-HMF.

Figure 6 provides a snapshot of the CFD simulation results we have generated, depicting the change in system phenomena - water volume fraction, pressure, and temperature distributions - with time in the laboratory scale BPR. Coupling the sucrose conversion kinetic model from above (Figure 5) with the CFD model below enables the performance of the laboratory scale and outdoor BPR systems to be predicted and the optimum performance conditions to be identified.

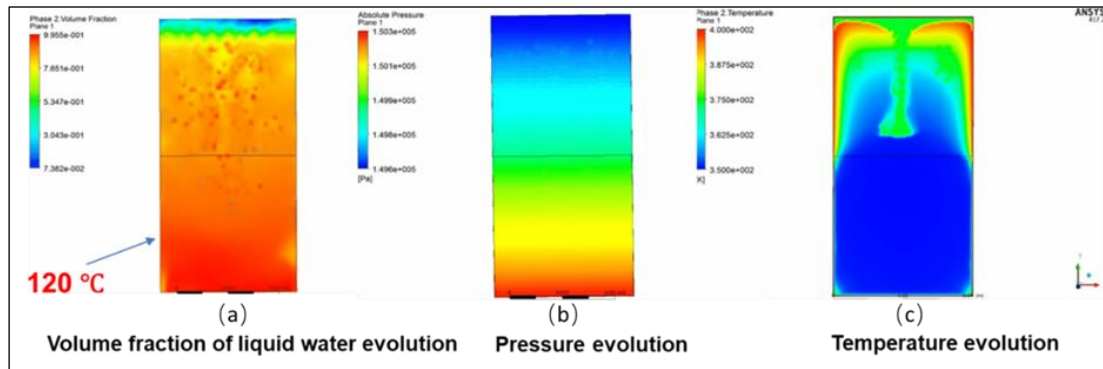


Figure 6: A snapshot of CFD simulation results describing the change in phenomena: (a) water volume fraction distribution; (b) pressure distribution; (c) temperature distribution; with time during sucrose conversion to 5-HMF (and other intermediates) in the laboratory scale BPR.

FEC model development and validation

A three-dimensional transient CFD model for the laboratory scale FEC has been developed. In this system, the electrochemical reactions occurring during the electrolysis process and species separation (e.g. hydrogen) by the membrane in the MEA have been modelled for the first time. The established model can now be used to understand and optimise processes in relation to the structure of specific FEC components. For instance, the model can be used to design/tune liquid flow channels and the gas diffusion layer (GDL) in the FEC system.

A base CFD electrolyser model has been developed and used to define typical in-electrolyser phenomena relating to electrolysis in the system as shown in Figure 7. Phenomena such as the electric potential (Figure 7(a)) and current density (Figure 7(d)) imposed on the electrodes, as well as the mass transfer behaviours of hydrogen (Figure 7(b)) and oxygen (Figure 7(c)) driven by the electrolysis process can be predicted.

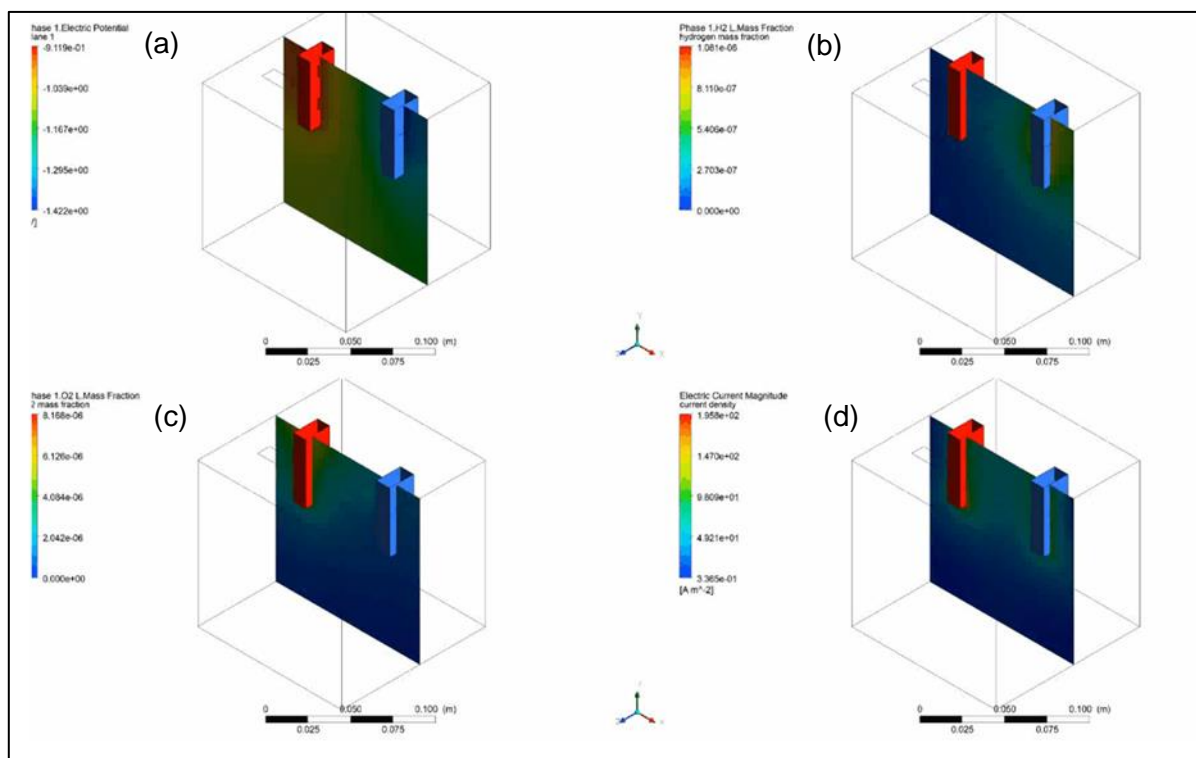


Figure 7: In-electrolyser phenomena relating to electrolysis in the simplified electrolyser model: (a) electric potential; (b) hydrogen mass transfer; (c) oxygen mass transfer; (d) current density

The next stage in terms of updating the model involved introducing the function of the membrane between the two electrodes. The membrane controls hydroxide (OH^-) transfer in the electrolyte flow. Figure 8 provides the model output describing the flow regime. Species transfer occurred on both sides of membrane - H_2 on cathode side, O_2 on anode

side - where only the hydroxide passes through membrane from the cathode side and approaches the anode. Implementation of the membrane function bridged the final gap whereby the FEC system can now be comprehensively modelled.

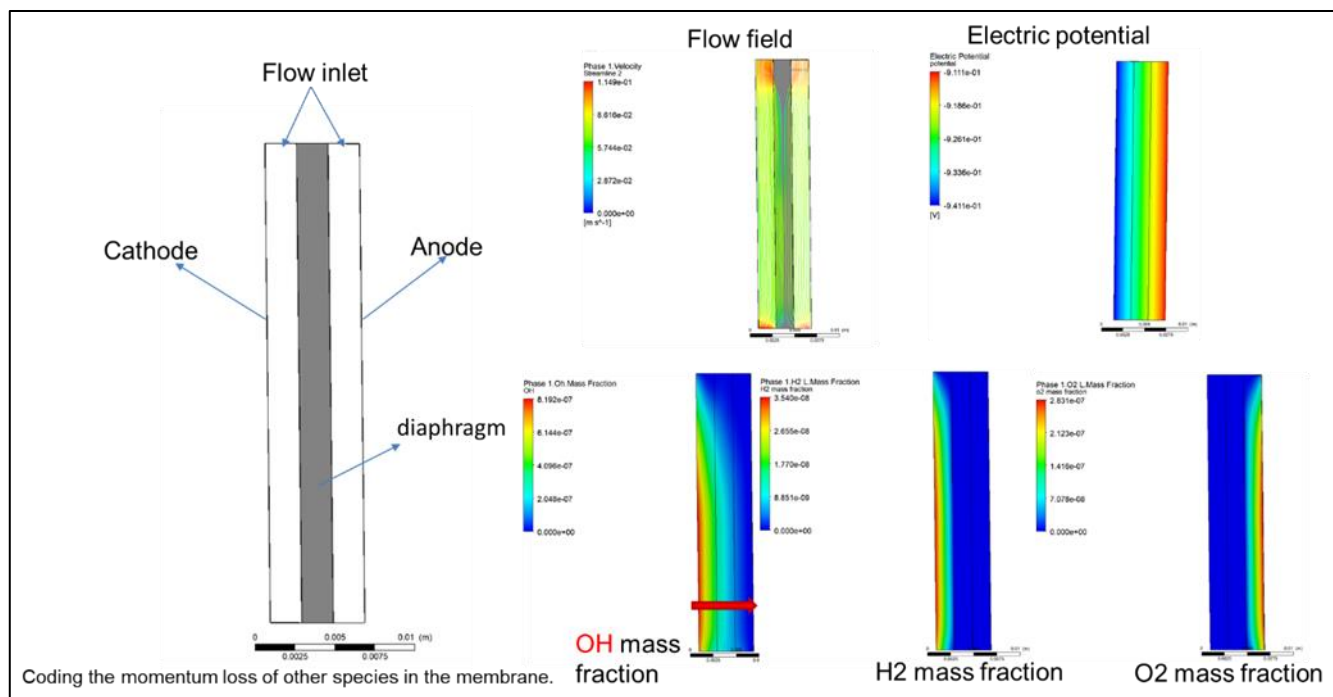


Figure 8: Simulation results under assumed operating conditions in the FEC system model: (a) schematic of anode, cathode and membrane arrangement; (b) flow regime; (c) electric potential; (d) hydroxide ion diffusion; (e) hydrogen mass transfer (from cathode); (f) oxygen mass transfer (from anode)

COMMERCIALISATION PROSPECTS

In this project, a tandem system comprising a solar-thermal reactor unit (BPR) for conditioning biomass (into a form more amenable for H₂ extraction) is joined with an electrocatalytic cell (FEC) capable of extracting the H₂ from the pre-conditioned biomass is being developed and scaled to a prototype level. In conjunction with infrastructure design, new catalyst materials are being designed (for both the BPR (TiO₂-ZrO₂ composite) and the FEC (supported Co hydroxide)) and a computational model is being developed which will assist with providing insights and scaling the system overall.

Using biomass as a H₂ source in an electrolytic system has many advantages, from energy to economic perspectives. Biomass molecules, such as sugar- or fat-derived alcohols, can be produced at very low cost from raw biomass streams (e.g. sugars and vegetable oils in waste) and they generally have a very low standard oxidation potential (< 0.2 V) compared to water oxidation (1.23 V); which is < 80% of what is required for water electrolysis. That is, only < 0.5 kWh is required to produce one m³ of H₂ using biomass-derived alcohols. It is projected that a biomass-based electrolytic cell will consume less than half of the energy (0.8 V for bio-alcohol versus 1.8–2.0 V for water) needed for a commercial water electrolyser.

Based on the results to date, coupling the performance of the BPR (~17% yield (0.034 M) from 100 mL of 0.1 M sucrose solution) and the FEC (~26.6 mL of hydrogen from 50 mL of a 10 mM 5-HMF solution) and scaling the FEC system to 1L capacity sees an output of 18.1 mL of hydrogen produced per 1 L of 0.1 M sucrose solution. Combined, the findings demonstrate the tandem BPR-FEC system is able to extract hydrogen from biomass. The findings imply that, at this stage the project successfully achieves the project deliverables (advancing technology from TRL3 to TRL4) in the path towards commercialisation.

SUMMARY OF KNOWLEDGE SHARING ACTIVITIES COMPLETED

- CIs Scott, Taylor and the RAs met with a delegation from Nanjing Tech University (China) on 24/05/2019 where details on the ARENA hydrogen-from-biomass technology project were presented. They were on a fact-finding trip and were interested in details on projects in the areas of biomass, solar, and hydrogen technologies.

- The project CIs and RAs met with Ken Baxter (Energy Advisor, Innovation and Partnerships) and colleagues from Melbourne Water on 26/06/2019. Melbourne Water was interested in the biomass treatment system being developed for extracting hydrogen from their municipal waste sludge streams and reached out after seeing the project on the ARENA website. The outcome from the discussion was Melbourne Water was willing to provide waste sludge samples (on the basis of all associated risks being identified and accounted for) at a time when the project was ready to move from using the control biomass (sucrose) to examining a real biomass waste sample.
- CIs Scott and Wang met with Chris Williams and Steve Ward from Canvas Events (www.canvasevents.com.au) on 18/12/2019 to discuss renewable hydrogen and energy technologies. Specifically, they were interested in learning of areas and potential technologies/R&D at UNSW which they could potentially embrace in their current/future business around energy and waste. The meeting focussed on describing the technology being developed from the biomass project and how it may be integrated into their business in the future.
- The CEO of Apricus Energy (Victoria-based Industry Partner), Mick Humphreys, was invited to join the Biomass Project Team meeting on 29/07/2019. He travelled to UNSW to attend an in-person project meeting where we discussed his solar-thermal business/technology, his company's needs, and what he can contribute to the project going forward.
- CIs Scott, Wang, Bedford and Amal met with Dr Max Temminghoff and Dr Vivek Srinivasan from CSIRO Futures Group on 16/05/2019. Delivered presentation outlining concept of ARENA Waste Biomass to Renewable Hydrogen project.
- CI Scott invited by Dr Vivek Srinivasan (CSIRO Futures Group) to participate in CSIRO Hydrogen RD&D Opportunities Steering Committee from May-Dec 2019. CSIRO report: "Hydrogen Research, Development and Demonstration: Opportunities and Priorities for Australia" released in Dec. 2019. CI Scott attended report launch in Melbourne on 05/12/2019. The report can be found at www.csiro.au/en/Showcase/Hydrogen.
- CI Scott attended the CSIRO Hydrogen Industry Mission Briefing, held in Melbourne on 06/02/2020. Subsequently, on 11/03/2020, he submitted an Expression of Intent (with CI Amal and Prof. Aguey-Zinsou (UNSW)) in support of the CSIRO Hydrogen Industry Mission.
- The Ph.D. student William Hadinata Lie (externally funded Ph.D. stipend) participated in the UNSW Three Minute Thesis (3MT) competition, describing his work on the FEC component of the project. Research undertaken in the Ph.D. by William has been associated with electrocatalyst design for the FEC system in the project. He was nominated as the best presentation from the School (Chemical Engineering) where he was then runner up the next round (Faculty of Engineering level).
- CIs Scott, Wang and Amal are members of the Conference Committee for the 4th Energy Futures (EF4) Conference. The conference was due to be held in Sydney on 27-29 May 2020. At this stage, due to COVID-19, the conference has been tentatively postponed to February 2021. EF4 includes Themes of Renewable Hydrogen and Energy Conversion amongst others. The website can be found at www.ausenergyfuture.com.