Master Thesis Proposal
Building the Hydrogen Storage Infrastructure in the Arabian Gulf Region using Metal-Organic Frameworks

Domenico Lahaye[1], Valentina Olabi[2] and Rudy Paiman Sadi[3]
[1] *Delft Institute of Applied Mathematics, Technical University of Delft; d.j.p.lahaye@tudelft.nl*
[2] *Gulf Petrochemical Chemical Association; valentina@gpca.org.ae*
[3] *Almajdouie - de Rijke, Kingdom of Saudi Arabia; sadirp@almajdouie.com*

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1 Introduction

The aim of this Master's thesis project is to accelerate the deployment of sustainable fuels, namely hydrogen, in the Arabian Gulf region (Saudi Arabia, UAE, Oman, Qatar, Kuwait, Bahrain). This includes the design for sustainable infrastructure for the transport, storage and distribution of hydrogen, as well as the role of renewables in expediting hydrogen implementation in the region [3]. Mathematical modeling techniques and numerical simulation tools are expected to provide indispensable insight in comparing various scenarios.

In the Arabian Gulf, the joint use of solar and wind energy is expected to play a crucial role in the production of sustainable hydrogen as an alternative energy source. Hydrogen opens the perspectives to replace hydro-carbon fuels and to allow for clean combustion without pollutant formation. This combustion can supply energy in various ways. It can generate heat (household boilers (see e.g. Bekaert or Bosch domestic boilers)), drive the generation of electricity (see e.g. recent studies on (micro) gas turbine engines) and be used as a fuel in internal combustion engines or fuel cells for cars and trucks (see recent work at the Polytechnic University of Milan (see e.g. the presentation by T. Lucchini at 18th OpenFoam workshop Genua) or Warttha Finland (see presentation Mild Combustion Workshop in Naples in 2022)). Hydrogen, however, has a small molecular size and low density. The storage of hydrogen (at e.g. low temperatures and high pressure) is therefore a well-known technical challenge.

This project intends to study solutions for the storage of hydrogen. Both small (individual households, personalized trasnsport) and large scale storage (industrial, residential, mass transport) systems can be examined (quantify small and large, amount of hydrogen fuel and storage capacity). The batteries proposed will be adapted to local circumstances in the Arab Gulf. Here solar energy is abundantly available in large flat dessert areas. This energy can be harnessed to produce, store and discharge hydrogen.

This project aims to investigate alternative hydrogen utilisation and storage techniques in the Arabian Gulf region. In Section 2, we give an overview of existing hydrogen storage techniques. In Section 3, we describe the utilisation of Metal Organic Frameworks (MOFs) as the potential future solution to wide-scale hydrogen storage.

2 Overview of Existing Hydrogen Utilisation and Storage Technologies

Here we give on overview of existing hydrogen utilisation and storage technologies (see e.g. https://en.wikipedia.org/wiki/Hydrogen_storage for more information).

1. **mechanical storage**: the compression of hydrogen into large cylinders at high temperatures and low pressures (cryogenic storage) is currently the most utilised manner to store hydrogen in liquid form. This method utilises cylinders composed of either metals or specialised plastics to store hydrogen. Decompression and heating then releases this stored hydrogen for use;

2. **chemical bonding**: hydrogen can be produced for end-use through the cracking of ammonia over a cobalt catalyst. This method presents several advantages, including that the hydrogen can be extracted at low pressures and moderate temperatures. The hydrogen produced from the cracking is released by the decomposition of the ammonia (this involves the heating or de-bonding of the ammonia);

3. **storage via adsorption**: the physical bonding of hydrogen to a variety of solid materials with high surface areas has also been investigated by means of the Brunaner-Emmett-Teller (BET) theory (see e.g. https://en.wikipedia.org/wiki/BET_theory for more information). These materials present the advantages of being able to adsorb hydrogen at low pressures and moderate temperatures. However, majority of assessed materials is that they adsorb hydrogen at too low of a capacity to be able to be implemented for wide scale use. Metal Organic Frameworks (MOFs) belong to this category of solid materials.

3 Hydrogen Storage Using Metal-Organic Frameworks

Here we describe hydrogen storage using metal-organic frameworks (see e.g. https://en.wikipedia.org/wiki/Metal%E2%80%93organic_framework and its section *Hydrogen Storage* for more information, [1], [2] and [5]).

Metal-Organic Foams A metal–organic framework is an organic-inorganic porous extended structure. (to be extended)

Hydrogen Storage using Metal-Organic Foams

1. fill container with a metal-organic framework (dimensions?; type of metal-organic material?)
2. describe physics of charging container with hydrogen when available. Assuming reactor to be perfectly mixed. Modeling in time, assuming no spatial distribution. Three phases. Phase 1 or M-phase: hydrogen absorption by metal-organic material. Phase 2 or M+MH: nucleation process, formation of 2-phase system in which M and MH co-exist. Phase 3 or MH phase in which M-phase disappears.
3. dis-charge container when the stored hydrogen is required;

Drivers for Mathematical Modeling and Numerical Simulation The project wishes to develop mathematical modeling and numerical simulation tool as a means to answer the following research questions

1. how does the *filling rate* depend on factors such as pressure and temperature in the battery, size of the battery and type of metal-hydrides used?
2. what is the *absorbed capacity* in kg.H2/ltrs or kg.H2/kg.adsorbent?
3. what *discharge rate* can be expected?
4. what is the adsorbent utilization considering filing and discharge cycle? In other words, can a container be discharged at 100%?
5. what is the expected filling/discharge cycle? In other words, how will the adsorption efficiency deteriorate over time?

Recent Insights

- Ti-MOF-16 technology most promissing: see https://www.pv-magazine.com/2022/09/02/hydrogen-storage-techniques/;
- request for upscaling from applications seen last;

4 This Project Subdivided in Stages

The project is expected to be carried out in the following four stages.

4.1 Literature Study

The goal of the literature study is to provide broader and deeper context to the ideas introduced above. Fine in case that (parts of) the literature study are descriptive and/or speculative. Deliverable is literature study report that will be shared among project partners.

4.2 Perfectly Mixed Reactor Model for Battery (Dis)Charging

The goal of this project stage is to develop a first mathematical model for the (dis)charging of the battery over time. The battery will be modeled as a perfectly stirred reactor. This model excludes spatial variations in the reactor. The model will describe the intake of hydrogen, the nucleation of the metal hydrides, and the consumption of metal oxide over the (dis)charging cycle. The role of the thermodynamics (temperature and pressure) and the kinetics (type of metal-oxide, surface area, reactivity) will be taken into account. A set of coupled ordinary differential equations that describe the time-evolution of the concentration of unbounded hydrogen, bounded hydrogen and available metal-oxide will be formulated and solved numerically. One option here is to adopt the Julia programming language (see `julialang.org`) given its smooth learning curve and the availability of renouwed package `DifferentialEquations.jl` to solve ordinary differential equations. Deliverable is a piece of public-domain software shared via github that solves model numerically.

4.3 Compartimental Reactor Model for Battery (Dis)Charging

The goal of this project stage in to extended the model developed in the previous stage with model physical realism. Spatial variations in the reactor (in 1D, 2D and 3D) will be taken into account. A set of time-dependent conservation equations for the concentration of hydrogen and metal hydrides will be formulated and solved numerically. An option here is to adopt a package for solving partial differential equations in Julia (`Gridap.jl`, `Ferrite.jl`, `Trixi.jl` or other). Deliverable is again a piece of public-domain software shared via github that solves model numerically.

4.4 Final Report and Presentation

Write final report and deliver final presentation.

5 Request for Funding

TU Delft requests a fund of 16kEUR subdivided in two parts as described as follows:

- fund of 6kEUR enabling two TU Delft master students to be hired as teaching assistant for 100 (hundred) hours per student (200 hours in total);
- fund of 10kEUR enabling two master student and two supervisors to study visit the Arabian Gulf region in the context of the project;

6 Non-Disclore Agreement

Non applicable in first stage of the project. Might change as the project evolves.

7 References

1. D. P. Broom *Hydrogen Storage Materials - The Characterisation of Their Storage Poperties*, Springer 2011.

2. J. Graetz, *New Approaches to Hydrogen Storage*, Chemical Society Reviews, 2008.

3. Valentina Olabi, *The Rise of Hydrogen - Fueling a Green Revolution*, Gulf Petrochemical Chemical Association (gpca.org)

4. S. Rogge e.a. *Modeling Gas Absorption in Flexible Metal-Organic Frameworks via Hybrid Monte-Carlo/Molecular Dynamics Schemes*, 2019. Advances Theory and Simulations,

5. A. Züttel, *Materials for Hydrogen Storage*, Materials Today, September 2003.