CHEMICAL ENGINEERING TRANSACTIONS

VOL. 90, 2022

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Aleš Bernatík, Bruno Fabiano

ISBN 978-88-95608-88-4; **ISSN** 2283-9216

DOI: 10.3303/CET2290010

Green Hydrogen Production Routes: a Inherent Safety Assessment

Mariasole Cipolletta*, Valeria Casson Moreno, Valerio Cozzani

Alma Mater Studiorum - Università di Bologna, Department of Civil, Chemical, Environmental and Materials Engineering, via Terracini 28, 40131 Bologna, Italy
mariasole.cipolletta@unibo.it

In the framework of energy transition, safety is a key requirement to be satisfied by novel process technologies. The aim of this study is to compare, from an inherent safety standpoint, three technologies for the production of green hydrogen via water splitting, powered by Renewable Energy Sources (RESs), in order to identify the inherently safest option and the critical equipment and/or operating conditions to be considered in the scale-up and industrialization of such technologies. The technologies considered for green hydrogen production are: alkaline electrolysis, proton exchange membrane electrolysis and reversible Solid Oxide Cells. The application of a consolidated methodology for inherent safety assessment based on Inherent Safety Key Performance Indicators (IS-KPIs) enabled to identify the most critical units within each process scheme and to select the inherently safest technological solution presently available for green hydrogen production.

1. Introduction

Hydrogen attractiveness has made it the gravitational centre of the present energy transition, with green hydrogen, i.e. hydrogen produced by RESs-powered water electrolysis, occupying the leading role towards a carbon-neutral society (Kovač et al., 2021).

In fact, hydrogen has an extremely high versatility in the field of chemical energy storage, being the basic intermediate or final product for almost any Power-to-X (PtX) process, but also being itself an intermediate for Power-to-X-to-Power (PtXtP) systems (Venkataraman et al., 2019). In the latter solution, excess electrical energy produced through RESs is stored in the form of chemicals which are converted back to power when needed.

In this framework, hydrogen is the most feasible chemical for the purpose of energy storage, competing directly with solutions as pumped hydro storage, compressed air storage and batteries (Venkataraman et al., 2019).

Thus, even if mature technologies for electrolysis are available, innovation is making the pace of optimization efforts extremely rapid in order to improve provide novel water-splitting strategies and conditions that could improve the overall energy efficiency of the system.

At present, two technologies dominate the market: alkaline electrolysis (AEL) and proton exchange membrane (PEM) electrolysis. AEL is already proved for large-scale and durable applications, demonstrating lower CAPEX and maintenance costs, while PEM electrolysers can be preferred due to their nimbleness in following power dynamics (Rizwan et al., 2021).

Recently, reversible Solid Oxide Cells (rSOC) were proposed for water electrolysis as a promising technology improving the hydrogen yield by means of a lower electricity consumption than the consolidate ones (Xiang et al., 2016). The higher efficiency of rSOC is in their capacity to produce hydrogen at lower voltage tenors, due to the O_2^- transport that the ceramic membrane performs and the improved reaction kinetics resulting from processing steam (Ju et al., 2018). Furthermore, differently from AEL and PEM technologies, rSOC have a double mode of operation, enabling both electrolysis as Solid Oxide Electrolysis Cells (SOEC) and combustion operation as Solid Oxids Fuel Cells (SOFC), therefore complying to the eventual need of flexible applications as PtXtP and lowering the capital costs of the facility (Venkataraman et al., 2019). Furthermore this technology appears suitable for heat integration and it is prone to be paired with other process facilities for synergy (Ju et al., 2018).

Paper Received: 27 January 2022; Revised: 24 March 2022; Accepted: 25 April 2022
Please cite this article as: Cipolletta M., Casson Moreno V., Cozzani V., 2022, Green Hydrogen Production Routes: an Inherent Safety Assessment, Chemical Engineering Transactions, 90, 55-60 DOI:10.3303/CET2290010

Hydrogen is extremely hazardous in terms of flammability, and in case of RESs-driven electrolysers with dynamic loads, the gas crossover phenomena is difficult to be prevented so that full load operation is always preferred (Yao et al., 2021).

Hydrogen hazards are extremely well-known in process industry and fatal incidents related to its unwanted releases in the last 20 years have a higher occurrence rate than for methane (Yang et al., 2021). During the design of process plants, the assessment of process safety thus cannot be disregarded, in order to apply as far as possible prevention actions by means of proper design considerations and choices. Thus, assessing the inherent safety of a process technology provides an early identification of hazards and risky operations, providing selection criteria among alternative process technologies and eventually suggesting modifications to the schemes in the early design steps (Gao et al., 2021). Safety evaluations on systems handling H_2 and studies predicting its strong flammability behaviour abound in literature (Jeon and Kim, 2020). Numerical simulation of H_2 gaseous mixtures from reaction equipment is very often addressed as to identify the actions to be performed in detail on known configurations and plants as performed by Zhang et al. (2021) and Priambodo et al. (2021). Tugnoli et al. (2009) studied H_2 throughout its supply chain; the same research group also assessed the inherent safety of conventional hydrogen production from steam reforming of natural gas (Tugnoli et al., 2008) and of hydrogen storage facilities (Landucci et al., 2008).

However recent research lacks in the evaluation of the inherent safety status of those technologies aimed at green hydrogen production. Therefore, this contribution aims at filling this gap through an inherent safety assessment run over the alkaline, PEM and reversible Solid Oxide Cells electrolysis.

2. Methodology

To run the safety analysis on green hydrogen technologies, Inherent Safety Key-Performance Indicators (IS-KPIs) as introduced by Tugnoli et al. (2007) were applied. The conceptual design of the process scheme for each electrolysis process is performed on the base of a fixed productivity, which is here chosen as the hydrogen flowrate obtainable by AEL electrolysis when powered by 3 MW steady-state power, which represents a typical size for the studied process. The procedure starts with the definition of the stack prototype from available technical sheets of constructors/providers. It is assumed to design the balance of plant (BoP) as shared among the eventual parallel lines of stacks and since this configuration resulted equivalent to setting separate BoP for each stack parallel line according to Rizwan et al. (2021). Specifications applied to produced hydrogen are: final purity of 99.9 % on molar basis and storage conditions of 30 °C and 150 bar.

Optimal process operating conditions and parameters were identified for each process by means of the Aspen HYSYS v.10 software (AspenTech, 2020). Preliminary equipment design was carried out and chemical inventories were calculated in order to identify the Potentially Hazardous Equipment (PHE). KOH was disregarded in this study, as limit concentrations causing irreversible damages to humans are not defined. Furthermore, a 30 %w/w solution is used, therefore hydrogen was the only hazardous substance to be analysed.

Three types of critical events involving the loss of containment of the equipment are associated to each PHE (Uijt de Haag and Ale, 1999): catastrophic rupture, large and small bores (LOC 1, 2 and 3 respectively).

The releases are then simulated by the application of source term models to quantify the flowrates (Van den Bosch et al., 1997) while Credit Factors (C_fs), representing the yearly occurrence frequencies, are assigned to each LOC. C_fs are obtained from baseline frequency values suggested for equipment failure, as per Uijt de Haag and Ale (1999).

Then Release Accident Scenarios (RASs) deriving from the critical events are identified by means of event trees which are associated to the j-th LOC considered for the i-th unit.

Each RAS effect is quantified through the evaluation of its related damage distance (DD), which is the distance at which the consequences of the scenario of concern equal a threshold value for the human target, which is specific for each dangerous phenomenon (radiation, overpressure, toxic concentration). The threshold values for fires, explosions and toxic clouds are reported by Tugnoli et al. (2007).

For the calculation of the DDs, the software PHAST v.6.5.4 (DNV-GL, 2020) for consequences evaluation is used, applying reference environmental conditions (average wind speed of 1.5 m/s, Pasquill category F (i.e. night time, air temperature of 25 °C with 70 % of relative humidity, and surface temperature of 10 °C). Hazardous inventories less than 0.5 kg cannot simulated by the software; effects were registered at 1 m height from the ground level. Then after, Inherent Safety Key Performance Indicators (IS-KPIs) are calculated for the i-th PHE as in Eqs. 1 and 2. The Unit Potential hazard Index (UPI_i) [m^2] is based on the comparison of all maximum damage distances $h_{i,j}$ associated to the i-th PHE and derived by any j-th LOC, thus this indicator is a metric of the maximum impact area that could be affected by the worst-case scenario generated by the i-th PHE. The Unit inherent Hazard Index (UHI_i) [m^2/y] considers also the likelihood of the release scenario by means of the C_fs, thus being an expression of the risk associated to the equipment item.

$$UPI_i = \pi \, max_j\left({h_{i,j}}^2\right) \tag{1}$$

$$UHI_i = \pi \sum_j^{\mathrm{LOC}} C_{fi,j} \cdot {h_{i,j}}^2 \tag{2}$$

Finally, the unit metrics are unified in overall process IS-KPIs, namely PI and HI, through a summation on all PHEs identified, which allow the discussion of the inherent safety performances of the process alternatives and their ranking.

3. Process Schemes

The design of the three electrolytic processes was based on a hydrogen productivity equal to 60.8 kg/h and on the operative parameters summarized in Table 1. AEL process design was based on the optimised operating conditions and stack performance as reported by Rizwan et al. (2021). The electrolytic process via PEM was set according to the average operating conditions of the PEM cells as reported by Shiva Kumar and Himabindu (2019) and Panchenko et al. (2019). The electrolysis process based on rSOC was set considering the results obtained for the system operating in electrolysis mode by Mottaghizadeh et al. (2017).

Table 1: Operative conditions set for the three electrolysis processes analysed.

	AEL	PEM	rSOC
H_2 produced [kg/h]	60.8	60.8	60.8
O_2 produced [kg/h]	486.7	486.7	486.7
Electrolyte solution fed [kg/h]	33629	-	-
KOH w/w	0.3	0	0
H_2O w/w	0.7	1	1
H_2O fed [kg/h]	-	78409	1244
Temperature [°C]	80	50	800
Pressure [bar]	30	50	10

The simplified process schemes are reported in Figure 1 and Figure 2, where PHEs, i.e. equipment containing hydrogen inventories, are highlighted. Although the operative conditions are much different, the overall process schemes are similar and foresee the water/electrolyte stream feed to the stack, the electrolysis reaction, the separation of the gaseous products from the liquid stream for recirculation, and a final section for hydrogen refining and conditioning to reach the required specifications. It can be noted that several operations are needed in the downstream of the rSOC process to bring the product to the final storage conditions from the ones at which it is synthetized (800 °C, 10 bar).

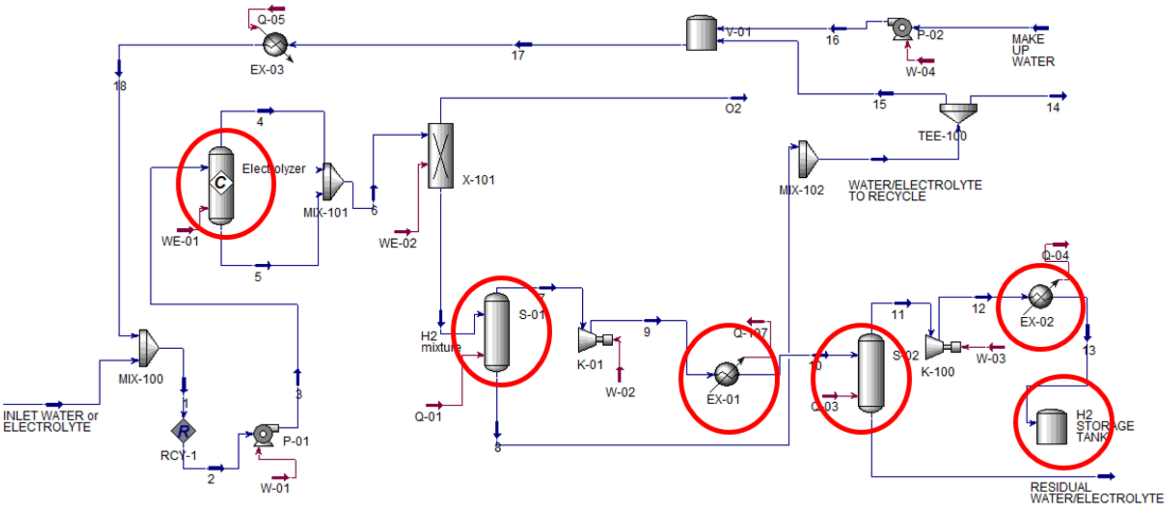

Figure 1: Simplified process scheme for AEL and PEM electrolysis. The highlighted equipment are PHEs.

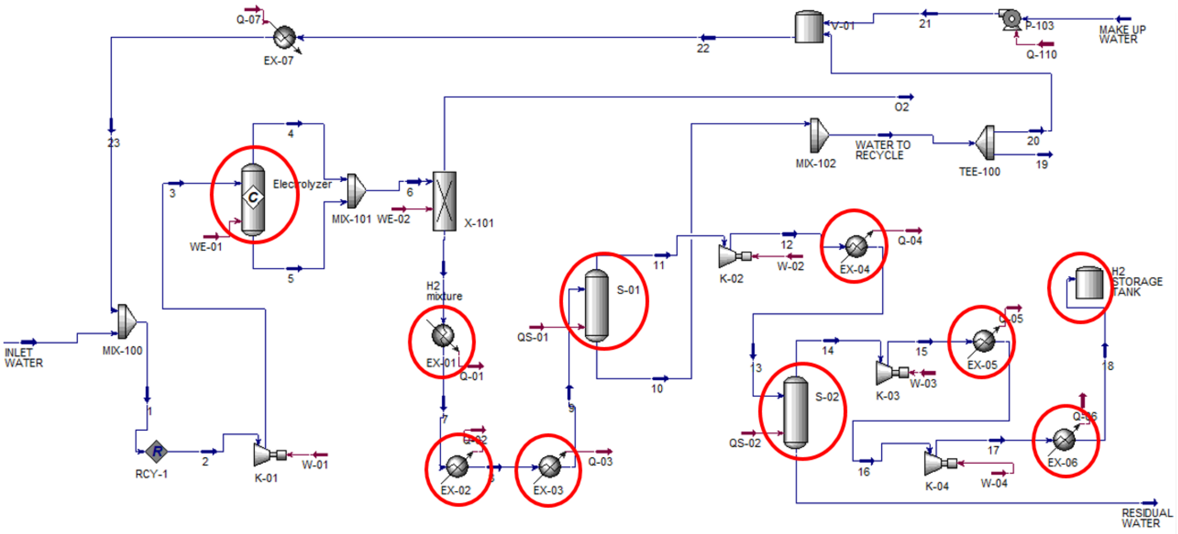

Figure 2: Simplified process scheme for rSOC electrolysis. The highlighted equipment are PHEs.

Table 2: Consequence assessment of the critical events considered for the PHEs identified in the three electrolysis processes.

Reference scheme	Equipment (T, P, H_2 inventory)	N of identical Items	Release characteristics			Damage Distances of RASs [m]			
			LOC	Mass or flow rate [kg or kg/s]	T [°C]	JET FIRE	FIREBALL	VCE	FLASH FIRE
AEL	ELECTROLYSER (80 °C, 30 bar, 67 kg)	1	1	67.0	-144.4	-	73.7	30.7	20.0
			2	0.1	72.1	14.0	-	3.8	11.2
			3	11.9	72.1	110.8	-	27.3	35.0
PEM	ELECTROLYSER (50 °C, 50 bar, 6.7 kg)	1	1	6.7	-173.2	-	35.6	10.2	8.6
			2	0.2	42.4	18.0	-	5.6	12.7
			3	20.5	42.4	141.0	-	13.9	35.3
rSOC	ELECTROLYSER (800 °C, 10 bar, 1.1 kg)	6	1	1.1	-97.4	-	20.1	-	4.6
			2	0.04	71.6	8.7	-	2.7	7.9
			3	4.2	71.6	69.6	-	7.8	22.7
rSOC	EX-03 (200 °C, 10 bar, 1.0 kg)	2	1	1.0	-34.9	-	19.5	-	4.4
			2	0.04	191.8	8.2	-	2.4	6.5
			3	3.6	191.8	65.1		7.6	19.5
All	H2 STORAGE TANK (30 °C, 150 bar, 26.4 kg)	1	1	26.4	-205.7	-	54.9	21.7	14.0
			2	0.6	24.9	29.1	-	9.1	18.2
			3	61.9	24.9	230.0	-	22.6	48.4

4. Results and discussion

Among the PHEs identified after process design and indicated in Figure 1 and Figure 2, only the LOCs related to the items reported in Table 2 were modelled since their hazardous inventory exceeded the minimum threshold amount for hazardous masses that can be simulated (0.5 kg). The electrolysers and the hydrogen storage tank are present as PHEs in all the processes, while in the rSOC scheme also the release consequences for the heat exchanger EX-03 were considered.

The RASs scenarios originated by critical events involving hydrogen are all related to fires. In the present study the worst damage distances are due to jet fires and fireballs, as shown in Table 2. The process conditions in the three schemes lead to the likelihood of occurrence of very severe jet fires, thus appropriate countermeasures should be considered to contrast the phenomenon, specifically considering the protection of the electrolysers

and of the storage tank, that resulted the most critical units. VCE are not very likely to occur, unless in case of congestion in the layout (e.g. offshore), as a consequence of the mass of hydrogen in the flammability range.
Despite the equivalence of the process principle, the inherent safety performances of the process alternatives are different, as shown in Figure 3. Both the Potential Index and Inherent Hazard Index are aligned in ranking the alternative technologies. The AEL is the inherently safest solution, followed by PEM electrolysis and by rSOC. Actually, due to the very high operating temperature of the solid oxides stack, this technology requires several equipment to cool down the hydrogen stream. Moreover, the low operating pressure requires more compression and inter-cooling steps to reach 150 bar for storage.

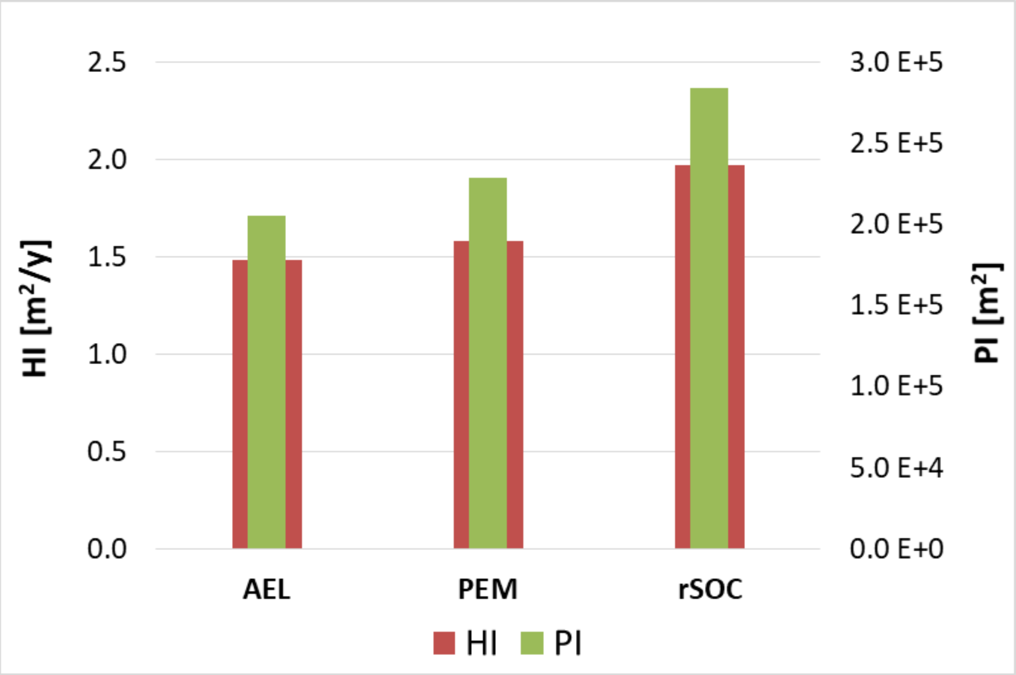

Figure 3. Inherent Safety Key Performance Indicators for the three electrolysis processes considered.

5. Conclusions

Renewable Energy Sources play a major role in decarbonizing the energy sector, enabling localized generation and the exploitation of unlimited natural fluxes. In this period of energy transition, R&D has a pioneer role in surpassing technological constraints, making novel generation systems widely approachable. Albeit hydrogen's promptness as fuel and the flexibility of its production routes, risks associated to plants' operation can't be neglected a priori because of its hazardous properties. Therefore, inherently safer solutions should be privileged for scale-up and industrialization. The assessment carried out, based on IS-KPIs, allowed identifying the risk factors and criticalities affecting reversible Solid Oxide Cells electrolysis as of more concern than those affecting conventional alkaline and PEM electrolysis.

References

AspenTech, 2020, Aspen HYSYS, version 11 <www.aspentech.com/en/products/engineering/aspen-hysys> accessed 04.01.2020.

DNV-GL, 2020, PHAST - Process Hazards Analysis Software, version 6.4 <www.dnvgl.com> accessed 04.01.2020.

Gao X., Abdul Raman A.Z., Hizaddin H.F., Bello M.M., Buthiyappan A., 2021, Review on the Inherently Safer Design for chemical processes: Past, present and future, Journal of Cleaner Production, 305, p. 127-154.

Jeon J., Kim S.J., 2020, Recent progress in hydrogen flammability prediction for the safe energy systems', Energies, 13(23), pp. 1-44.

Ju H.K., Badwal S., Giddey S., 2018, A comprehensive review of carbon and hydrocarbon assisted water electrolysis for hydrogen production, Applied Energy, 231, pp. 502–533.

Kovač A., Paranos M., Marciuš D., 2021, Hydrogen in energy transition: A review, International Journal of Hydrogen Energy, 46(16), pp. 10016–10035.

Landucci G., Tugnoli A., Cozzani V., 2008, Inherent safety key performance indicators for hydrogen storage systems, Journal of Hazardous Materials, 159, pp. 554–566.

Mottaghizadeh P., Santhanam S., Heddrich M.P., Friedrich K.A., Rinaldi F., 2017, Process modeling of a reversible solid oxide cell (r-SOC) energy storage system utilizing commercially available SOC reactor, Energy Conversion and Management, 142, pp. 477–493.

Panchenko O., Giesenberg L., Borgardt E., Zwaygardt W., Kardjilov N., Markötter H., Arlt T., Manke I., Müller M., Stolten D., Lehnert W., 2019, Influence of stoichiometry on the two-phase flow behavior of proton exchange membrane electrolysers, Energies, 12(3), pp. 1-12.

Priambodo D., Sunarko S., Purwanto W. W., 2021, Safety Investigation of Hazardous Materials Released from the Combined High Temperature Gas Cooled Reactor – Hydrogen Production Plant Using ALOHA Software, Atom Indonesia, 47(1), pp. 31–38.

Rizwan M., Alstad V., Jäschke, J, 2021, Design considerations for industrial water electrolyser plants, International Journal of Hydrogen Energy, 46(75), pp. 37120–37136.

Shiva Kumar S., Himabindu V, 2019, Hydrogen production by PEM water electrolysis – A review, Materials Science for Energy Technologies, 2(3), pp. 442–454.

Tugnoli A., Cozzani V., Landucci G, 2007, A Consequence Based Approach to the Quantitative Assessment of Inherent Safety, A.I. Chemical Engineering Journal, 53(12), pp. 3171–3182.

Tugnoli A., Landucci G., Cozzani V., 2008, Sustainability assessment of hydrogen production by steam reforming, International Journal of Hydrogen Energy, 33(16), pp. 4345–4357.

Tugnoli A., Landucci G., Cozzani V., 2009, Key Performance Indicators for Inherent Safety: Application to the Hydrogen Supply Chain, Process Safety Progress, 28(2), pp. 156–170.

Uijt de Haag P. A. M., Ale B. J. M, 1999, Guidelines for quantitative risk assessment (Purple Book), the Hague, Netherlands.

Van den Bosch C. J. H., Weterings R. A. P. M., TNO, 1997, Methods for the calculation of physical effects: due to releases of hazardous materials (liquids and gases), Yellow book, The Hague, Netherlands.

Venkataraman V., Pérez-Fortes M., Wang L., Hajimolana Y.S., Boigues-Muñoz C., Agostini A., McPhail S.J., Maréchal F., Van Herle J., Aravind P.V., 2019, Reversible solid oxide systems for energy and chemical applications – Review & perspectives', Journal of Energy Storage.

Xiang C., Papadantonakis K. M., Lewis N. S., 2016, Principles and implementations of electrolysis systems for water splitting, Materials Horizons, 3(3), pp. 169–173.

Yang F., Wang T., Deng X., Dang J., Huang Z., Hu S., Li Y., Ouyang M., 2021, Review on hydrogen safety issues: Incident statistics, hydrogen diffusion, and detonation process, International Journal of Hydrogen Energy, 46(61), pp. 31467–31488.

Yao M., Ge J., Sun B., Hu J., Koh S.W., Zhao Y., Fei J., Sun Z., Hong W., Chen Z., Hu W., Li H., 2021, Solar-driven hydrogen generation coupled with urea electrolysis by an oxygen vacancy-rich catalyst, Chemical Engineering Journal, 414, p. 128-753.

Zhang H., Sauerschell S., Ba Q., Hu G., Jordan T., Bajohr S., Xiao J., 2021, Numerical simulation of accidental released hazardous gas dispersion at a methanation plant using GASFLOW-MPI, International Journal of Hydrogen Energy, 46(2), pp. 2804–2823.