

INHERENT SAFETY ASSESSMENT OF PROTON EXCHANGE MEMBRANE (PEM) WATER ELECTROLYSIS FOR HYDROGEN PRODUCTION

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ABSTRACT

Hydrogen is increasingly recognized as a clean energy carrier and proton exchange membrane water electrolysis (PEMWE) has attracted significant attention as a pathway for green hydrogen production because of its ability to deliver high efficiency and rapid response. However, despite advancements in performance, the inherent safety aspects of PEMWE remain insufficiently addressed. Hydrogen is categorized under a wide flammability range, low ignition energy and risks of leakage, fire, explosion and corrosion that threaten its reliability. This project aims to identify and analyze potential hazards in PEMWE systems to evaluate their inherent safety level by using Heikkilä's Inherent Safety Index (ISI) and proposing design improvements based on the principles of inherent safety: minimization, substitution, moderation and simplification. The study applied ISI scoring for both chemical and process hazards by evaluating factors such as hydrogen-oxygen mixing, flammability, explosiveness, corrosiveness, inventory, pressure and equipment complexity. Results showed PEM to fall within the medium hazard category with hydrogen-oxygen mixing and corrosion as key concerns. Design improvements were proposed based on the four principles such as reducing hydrogen inventory, using corrosion-resistant materials, operating at lower pressures and simplifying stack design. Based on the findings, it demonstrated that inherent safety assessment provides a pathway to enhance PEMWE reliability and align with hydrogen production with industrial safety standards and sustainability goals.

Keywords: Hydrogen hazards; Proton Exchange Membrane Water Electrolysis (PEMWE); inherent safety; design improvement; process safety assessment.

1.0 INTRODUCTION

As the world's population continues to increase, more energy is needed to power industries, transportation, residences and businesses. Furthermore, in an effort to combat climate change, most of the countries have developed goals to reduce their carbon emissions. Greenhouse gases (GHGs) are released into the atmosphere when fossil fuels are burned, leading to the rising temperature of the Earth's surface and fostering the greenhouse effect. Therefore, this has led to a better alternative than fossil fuels by using a cleaner and renewable source of energy. Hydrogen is considered a promising alternative energy source because it does not produce greenhouse gases or other harmful emissions. By 2030, the global demand for hydrogen is expected. Among the most effective methods for producing clean hydrogen is proton exchange membrane water electrolysis (PEMWE). The water will be split into hydrogen and oxygen by using electricity. This process delivers several advantages such as, it is fast, efficient and does not create any pollution which helps to convince most countries and companies to invest in PEMWE and is expected to grow rapidly over the upcoming years.

Hydrogen is widely recognized as an ideal and propitious energy carrier due to its positive impact to the environment and world. However, behind the success and widespread usage of it, one of the most significant impacts that needs to be addressed is the safety concern present to ensure a safe production and storage of hydrogen. Therefore, it is important to improve hydrogen safety by doing research that leads to developing effective strategies, technologies and

rules that need to be highlighted because it has been a key concern for both developers and end-users. During hydrogen production by using PEMWE, there are several inherent hazards that must be studied. The causes of accidents will be associated with hydrogen systems which include system design, installation, human management and organizational management. The PEMWE system presents specific safety concerns, mainly arising from the characteristics of hydrogen (fast diffusion, low ignition energy, the tendency to cause hydrogen embrittlement, etc.) [1], high-pressure and dynamic operation characteristics, and purely electrical input (from renewables or the grid). The primary safety concern is the risk of fire or chemical explosions resulting from the combination of hydrogen with oxygen or air [2]. With an eye towards long term safety and reliability especially for PEMWE, the implementation of inherent safety principles is crucial. These principles help to eliminate, improve and modify to focus more on reducing the risk that will happen by addressing the hazards and doing risk assessment at the early stage of design rather than entirely depending on external control systems. Conducting a risk assessment will become not only relevant but obligatory to ensure public safety, investor confidence and regulatory compliance.

Therefore, the objectives of the study are to identify and analyze potential hazards in a PEMWE, and to evaluate the inherent safety level of the PEM electrolysis system and propose design improvements based on assessment methods and inherent safety principles. This study is mainly focused on performing a safety assessment of PEMWE systems by emphasizing a hazard identification during the early design phase. This part of the study aims to evaluate the inherent safety level of the PEMWE by applying and reviewing existing inherent safety assessment methods. In addition, a comprehensive literature review is conducted to gather relevant data on operating parameters, system design, and associated risks of PEMWE systems. The collected information served as the basis for applying inherent safety principles to develop a safer design for PEM water electrolysis.

2.0 METHODOLOGY

This section includes the flowchart of methodology, process overview, safety assessment framework and justification for the selection of methods and tools. A proactive approach is significant especially during the early design stage where the changes are easily made effectively and economically. The PEMWE is chosen as the operational system for this study because it offers clean hydrogen production and most importantly, there is currently a lack of comprehensive safety assessment focusing more on PEMWE. Given these observations, this study implements the Inherent Safety Index (ISI) by Heikkilä to evaluate the inherent safety of the PEMWE. ISI is an approach that integrates both chemical and process hazards such as flammability, toxicity, pressure, inventory and process complexity. Therefore, it is suitable for the early design stage where the process data may be limited. ISI is a simple method that does not require complex simulations and probabilistic data but remains practical. In order to assess the inherent safety of the PEMWE system for hydrogen production, a step-by-step methodology has been developed and illustrated in the form of flowchart. The flowchart ensures clarity in the execution of each stage for the safety assessment process started from process understanding until final analysis and validation. The methodology is mainly built on the application of the ISI. Below is the methodology flowchart that outlines the workflow of entire assessment process:

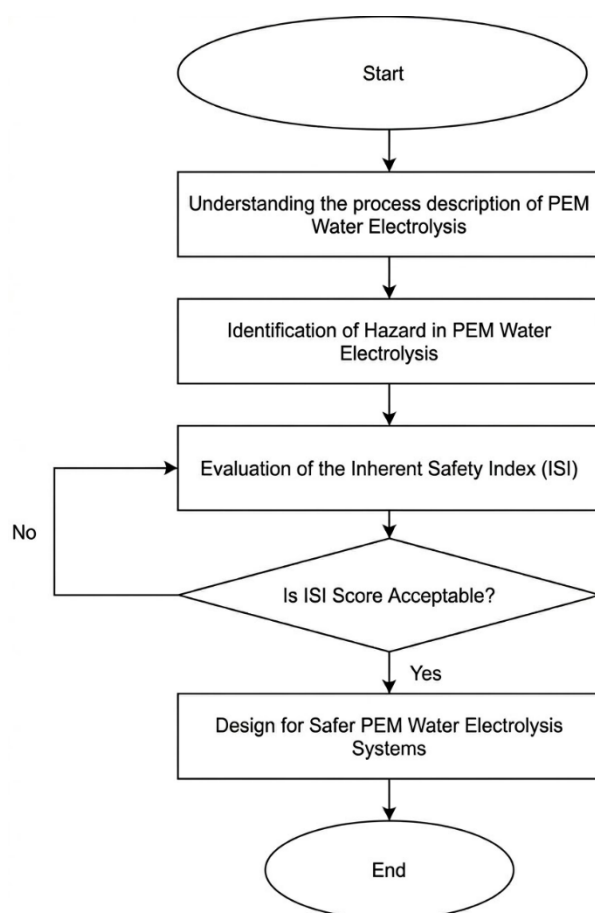


Figure 1. Methodological Flowchart for Inherent Safety Assessment of PEM Water Electrolysis

The study began with understanding in detail the working principle, process flow diagram, key components and operating conditions of the PEMWE. This step sets the foundation for hazard identification by understanding how the system functions. A solid grasp of the full process description ensures that the safety assessments can be done accurately and effectively.

Once the process was clearly understood, the next step involved hazard identification in the PEMWE system. This stage focused on systematically investigating all elements that may pose safety risks under both normal and abnormal operating conditions. This step is critical, as identifying where and how risks arise enables subsequent evaluation and the development of safer design alternatives. It represents the transition from system understanding to active risk assessment.

Following hazard identification, the study proceeded to evaluate the inherent safety level of the existing design using the method proposed by Heikkilä, namely the Inherent Safety Index (ISI). It is an assessment tool that assigns numerical values to represent the inherent safety level of chemicals and processes. A higher score indicates greater risk, whereas a lower ISI value reflects a safer and inherently low-risk system. The ISI method facilitates the identification of critical areas requiring improvement and greater attention during the design stage.

2.1 ISI Scoring

This stage played a crucial role in decision-making because it is a checkpoint to interpret the ISI results. The evaluation considered whether the calculated ISI score was sufficiently low for the PEMWE system to be regarded as inherently safe. A low score indicated that the current system design is acceptable, suitable and incorporates features that minimize and eliminate hazards. In this case, no changes may be needed, and the process was continued to the next step. This is because low scoring value indicates that all parameters and process equipment are suitable enough for the PEM Water Electrolysis to operate safely. However, if the total ISI score exhibited a high numerical value, it indicated that the system contained safety concerns requiring further attention. This decision point was critical, as it determined whether the next step involved re-evaluation or redesign.

For cases where the ISI value indicated a low level of risk, the study proceeded to the next stage, which involved designing a safer PEM water electrolysis system to further enhance inherent safety. The design phase applied inherent safety principles such as (1) Minimize, (2) Substitution, (3) Moderation and (4) Simplification. These principles eliminate and reduce the risk at the source rather than merely controlling them. To decrease the chance of operator error or mechanical failure, the design might be simplified to reduce complexity. This phase requires a lot of research because

decisions will be proposed based on the expert judgement to find safer alternatives without threatening the performance of PEM Water Electrolysis. This step not only serves to correct the existing safety issues but also implement safety into the process of the early design stage which leads to risk reduction.

The final stage concluded the inherent safety assessment which included the summarization of all findings, decisions and recommendations. This includes the initial process description, the identified hazards, the ISI scores and the outcomes of the redesign stage. It shows how the safety level has been improved as a result of implementing the inherent safety principles. This step highlights the importance of integrating inherent safety into the early stages of the design process rather than merely relying on add-on protective systems.

2.2 Process Description of Proton Exchange Membrane Water Electrolysis (PEMWE)

Proton Exchange Membrane (PEM) Water Electrolysis is an advanced hydrogen production technology that uses electrical energy to split water molecules into hydrogen and oxygen. From this process, green hydrogen which is safe for the environment can be obtained. This section will outline the working principle, components, operating conditions, production process and potential hazards of PEM Water Electrolysis.

2.2.1 Working Principle of PEMWE

A PEM electrolyzer cell comprises a membrane, two gas diffusion layers, two porous transport layers, and two bipolar plates with anodic and cathodic channels, as shown in Figure 2. The cell consists of two electrodes separated by a proton-conductive polymer membrane, which is typically Nafion. The process starts when water enters the cell and is supplied to the anode side. In this side (anode), water undergoes oxidation and is electrolyzed to produce oxygen, hydrogen ions and electrons. The hydrogen passes through the membrane to the cathode while the electrons travel to the external circuit and combine with hydrogen ions at the cathode to form hydrogen.

The reaction equations are as follows [3]:

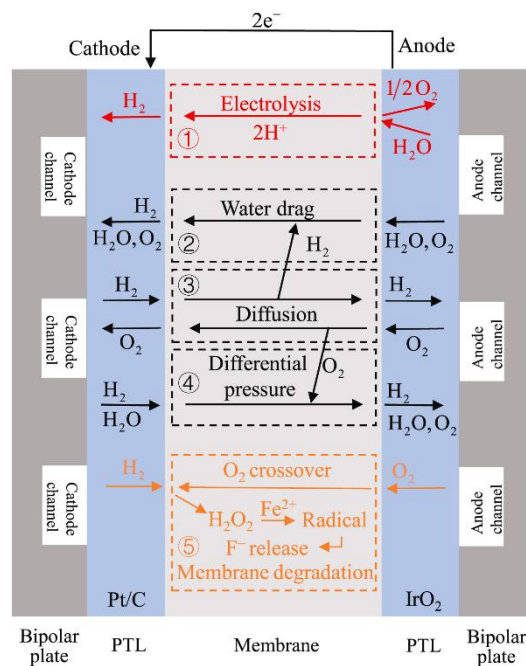


Figure 2. Schematic view of processes in the PEM Water Electrolysis [4]

According to Figure 2, its core components include a PEM electrolyzer and associated auxiliary system, with the process flow diagram of the system. In this study, the process flow diagram is adapted from a published journal article. The selected PFD as Figure 3 provides a clearer diagram because it shows more details of key components and flow paths which are important to identify the potential hazards.

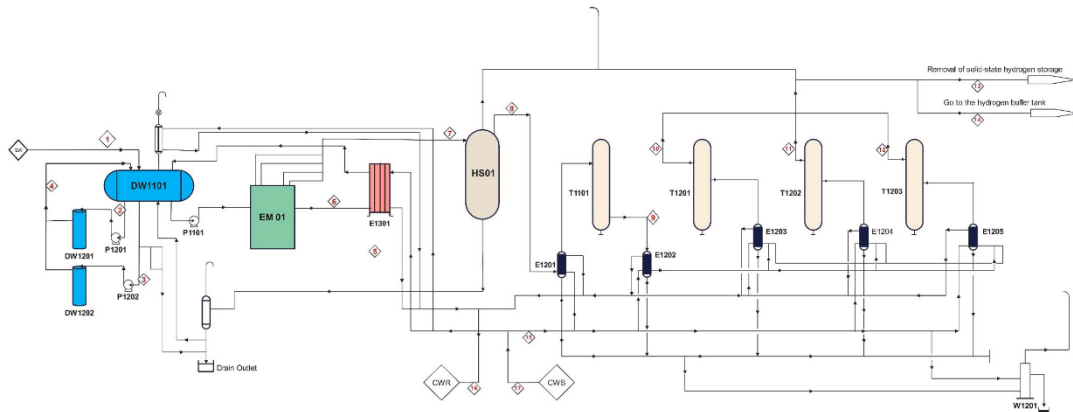


Figure 3. Process flow diagram of the PEM water electrolysis hydrogen production system [3]

2.3 Inherent Safety Assessment Approach (Heikkilä Method)

According to Heikkilä [5], the Inherent Safety Index (ISI) is divided into two categories, which are (1) Chemical Inherent Safety Index (CSI) and (2) Process Inherent Safety Index (PSI). Each category consists of several subindices that are evaluated individually and sum up to obtain the total index value.

(1) Chemical Inherent Safety Index (CSI)

As shown in Table 1, six subindices were considered for CSI and the calculation of the Chemical Inherent Safety Index, I_{CI} is presented in Equation (4).

Table 1. Factors selected for Chemical Inherent Safety Index (CSI)

Subindex	Description
Heat of reaction	During the reactions, energy will either be released or absorbed. Higher energy leads to higher hazards.
Flammability	The ability of a substance to ignite and sustain fire.
Explosiveness	The tendency to form explosive mixture
Toxicity	Harmful health effects from chemical exposure
Corrosiveness	The ability to degrade equipment and materials
Chemical interaction	Risk from reactions with other chemicals or materials

(2) Process Inherent Safety Index (PSI)

For the PSI, I_{PI} , another five subindices were considered, as shown in Table 2, and the corresponding calculation is presented in Equation (5). The total ISI index, I_{TI} was calculated as the sum of I_{CI} and I_{PI} as presented in Equation (6).

Table 2. Factors selected for Process Inherent Safety Index (PSI)

Subindex	Description
Inventory	Quantity of hazardous material circulating or stored in the process
Temperature	Higher temperature leads to high risks and hazards
Pressure	High pressure increases leak and explosion risks
Equipment Safety	Complexity and risk of failure in equipment design.
Process structure	Degree of process complexity and its impact on control and system

Chemical Inherent Safety Index, I_{CI}

$$I_{CI} = I_{RM,max} + I_{RS,max} + I_{INT,max} + (I_{FL} + I_{EX} + I_{TOX})_{max} + I_{COR,max} \tag{4}$$

Process Inherent Safety Index, I_{PI}

$$I_{PI} = I_I + I_{T,max} + I_{p,max} + I_{EQ,max} + I_{ST,max} \tag{5}$$

Total Inherent Safety Index, I_{TI}

$$I_{TI} = I_{CI} + I_{PI}$$

(6)

3.0 RESULTS AND DISCUSSION

3.1 Hazard Identification of PEMWE

Hazard identification is a critical step in any safety assessment, as it provides the foundation for evaluating risk levels and guiding design improvements. Table 3 shows the results of hazard identification of PEMWE, incorporating an analysis of its process operating conditions based on the literature.

Table 3. List of possible hazards in PEMWE

Category	Type of Hazard	Description
Chemical Hazard	Hydrogen flammability	<ul style="list-style-type: none"> Hydrogen has a broad flammability range (4–75 % in air), low ignition energy [6] Minimum ignition energy (MIE) is approximately 17μJ [7], nearly a tenth of that of gasoline. The MIE further drops to 5.7 μ J when air is enriched with oxygen by volume up to 35 % [8].
	Explosiveness	Gas mixing under high pressure is possible, where hydrogen permeation/crossover from the cathode side can cause hydrogen-oxygen mixing [9]
	Corrosiveness	Corrosion by hydrogen at high temperature [10]
	Hydrogen permeation	Hydrogen molecules are relatively small in size than other gases, hydrogen can permeate into other material more easily. The rate of permeation increases with higher temperature and storage pressure as well as aging of the material [10]
Process Hazard	Pressure hazards	PEMWE typically operates at 30–40 bar, increasing mechanical failure risk [9]
	Temperature hazards	PEMWE operates at range of 20 - 80 °C [11]
	Electrical hazards	High current densities (>2 A/cm ²) [11] can cause overheating and short circuits
	Gas crossover	Gas crossover is caused by structural defects of electrolyzer components as well as operating conditions [12]
	Inventory risks	Although hydrogen production via PEMWE is typically on-demand, keeping the actual internal inventory relatively low, it still presents a significant hazard. Depending on the power capacity and the number of cell units, reported hydrogen production rates range from 14 mL/min (at 4.3 W) [13] to 1.9 L/min (at 980 W) [14]. Even these small volumes pose severe inventory risks; because of hydrogen's wide flammability range and exceptionally low ignition energy, minor leaks in confined spaces can rapidly accumulate to explosive concentrations. Furthermore, if the generated hydrogen is not utilized immediately by a downstream application, such as a directly coupled fuel cell, it necessitates extremely high-pressure storage (typically 350–700 bar), which drastically elevates the external inventory hazard [15].
Material & Degradation Hazards	Membrane degradation	Proton exchange membranes, especially PFSA-based materials like Nafion degrade because harsh chemical environments, high temperatures, mechanical stress, water exposure at extreme conditions and electrochemical reactions break polymer chains and sulfonic acid groups, weakening the membrane structure [16].
	Catalyst poisoning	Catalyst poisoning in PEM water electrolysis occurs when impurities (such as CO, sulfur compounds, or metal ions) adsorb onto the catalyst surface, blocking active sites. Such a situation may lead to the generation of hot spots from the direct exothermic reaction of hydrogen and oxygen gases across the membrane and to internal short circuits due to cell failure [17].
	Corrosion of bipolar plates	Bipolar plates can corrode because of acidic conditions created by the proton exchange membrane and electrochemical reactions during operation [17].
External & Environmental Hazards	Ambient conditions	In poorly ventilated confined spaces, leaked hydrogen rapidly accumulates, forming a flammable layer. This creates an extreme explosive hazard, with gas concentrations reaching critical flammability levels within seconds. Scenarios with improper ventilation have recorded H ₂ concentrations approximately 50% higher compared to properly ventilated scenarios [18].

	Human factors	Operators may overlook small hydrogen leaks, which can accumulate and lead to explosions.
	Natural events	Fire, flood, or seismic activity can compromise containment

3.2 Inherent Safety Level of the PEM Electrolysis System

The Heikkilä's Inherent Safety Index (ISI) method provides scores that indicate the level of inherent risk in the system and highlight which parameters contribute most to that risk. The detailed scoring ranges for each sub-index are provided and justified in the supplementary information using the Heikkilä methodology [5]. Table 4 presents the results for ISI scoring data based on previous data. The data chosen is from the widest range.

Table 4. ISI Score Data

Chemical inherent safety index,	Typical PEMWE Value	Score	Justification
Heat of main reaction	Endothermic, $\Delta H = +285.8 \text{ kJ/mol}$ (15 870 J/g)	4	Extremely exothermic due to it exhibiting high heat of reaction [19].
Heat of side reaction, max	-	0	No hazard, side reaction is minimal.
Chemical interaction	-	3	Formation of flammable gas – H ₂ /O ₂ mixing risk. High hazard. Gas crossover can form explosive mixtures.
Flammability	T _{bp} = -253 °C	4	The flash point is not applicable since hydrogen is in the gas phase; use the boiling point. Very flammable since T _{bp} less than 35°C.
Explosiveness	Explosiveness (UEL-LEL) = 75 – 4 = 71 vol%	4	High hazard (Explosiveness > 70 vol%). Explosive mixtures are possible in confined spaces.
Toxic Exposure	-	0	No direct toxicity
Corrosiveness	-	2	Moderate hazard. Requires titanium or coated plates to prevent oxidation on the anode side.
Chemical Inherent Safety Index, I_{CI}		17	
Process inherent safety index,	Typical PEMWE Value	Score	Justification
Inventory	-	0	The amount stored is small but so while it's not dangerous at a large scale, it still requires basic safety measures.
Process temperature	80°C	1	Low hazard. Temperature is below 150 °C, but overheating risk exists.
Process pressure	40 bar	2	Moderate hazard. Process pressure is in the range of 25-50 bar.
Equipment safety (ISBL)	-	1	Include pumps to maintain a continuous supply of reactant water to PEM.
Equipment safety (OSBL)	-	2	Storing hydrogen requires either high-pressure compressors to reach 350–700 bar at ambient temperatures or cryogenic refrigeration systems to liquefy it at -253°C [15].
Safe process structure	-	3	Questionable, process configurations that raise safety concerns, even though no accidents have been reported yet
Process Inherent Safety Index, I_{PI}		9	
Total Inherent Safety Index, I_{TI} $I_{TI} = I_{CI} + I_{PI}$		26	

It is important to note that Heikkilä's Inherent Safety Index (ISI) method provides scoring criteria for individual sub-indices but does not prescribe a classification range for the total score. Therefore, to make the results more interpretable and to improve the efficiency of hazard-level comparisons, this study introduces a practical scoring range framework. Table 5 presents the ISI hazard level interpretation, divided into four levels (Low, Medium, High and Very High). This adaptation will allow the ISI results to be communicated more clearly.

Next, based on the ISI Hazard level interpretation, the total ISI score for PEMWE which is 26 falls under medium hazard where the hazards are significant, but design improvements are required. Inherently safer design principles

(Minimization, Substitution, Moderate and Simplify) should be applied to reduce risks related to Proton Exchange Membrane Water Electrolysis.

Table 5. ISI Hazard Level Interpretation

Total ISI Score	Hazard Level	Interpretation
0-15	Low hazard	Process is relatively safe - hazards are minimal and manageable
16-30	Medium hazard	Hazards are significant - design improvements and safeguards are required
31-45	High hazard	Process involves major risks - inherently safer design strategies are critical.
>45	Very high hazard	Extremely hazardous - process may be unacceptable without fundamental redesign.

3.3 Recommended Design Improvements of PEMWE

Given that the PEMWE process is classified as a medium-hazard process, several design improvements were proposed based on four inherent safety principles: minimization, substitution, moderation, and simplification (Table 6).

Table 6. Design Improvements of PEM Water Electrolysis

Principles	Description
Minimize	<ol style="list-style-type: none"> 1. Instead of storing a large amount of hydrogen, store it when needed only. For example, connect the electrolyzer to a fuel cell so hydrogen can be used immediately to generate electricity. 2. Instead of utilizing high-pressure gaseous buffer tanks, couple hydrogen generation via PEM with solid-state hydrogen storage (e.g., metal hydride storage beds) [20]. 3. Add a purge cycle so that the leftover hydrogen is removed and does not accumulate in pipes.
Substitute	<ol style="list-style-type: none"> 1. Instead of using stainless steel materials which are prone to corrosion, substitute it with corrosion-resistant materials like titanium nitride-coated bipolar plates. 2. Use reinforced polymer membranes (e.g., expanded polytetrafluoroethylene) that are mechanically stronger than unreinforced membranes. These can extend the PEM's lifetime by three to four times and offer superior resistance to degradation [21].
Moderate	<ol style="list-style-type: none"> 1. Instead of broadly lowering the overall system pressure (which compromises efficiency), implement active back-pressure regulators that ensure a near-zero pressure gradient ($\Delta P \approx 0$) across the membrane under all transient loads. 2. Reducing channel depth that benefits water and product emission, as larger depths cause heat accumulation and higher temperatures [22].
Simplify	<ol style="list-style-type: none"> 1. Simplify the process layout by removing any unnecessary equipment that may cause overheating or potential to leak. 2. Use standardized stack modules which are easy to maintain and replace. 3. Install safety instruments such as hydrogen detectors and automatic shutdown systems, so the process can respond to problems without any manual intervention.

The hazard identification results for PEMWE highlight that hydrogen flammability is the most critical chemical hazard. This is because hydrogen has a wide flammability range 4 – 75% in air and low minimum ignition energy (MIE) of approximately 17 μJ . This risk is further raised when oxygen enrichment happens because the MIE can drop to 5.7 μJ at 35% oxygen concentration. These properties indicate that small leaks of hydrogen can easily ignite and flammability as the most risk hazards in PEMWE systems. Apart from that, explosiveness is also a major concern as hydrogen crossover through membranes or leaks from pipelines can lead to hydrogen-oxygen mixing, creating explosive mixtures. Hydrogen embrittlement and overpressure incidents further increased the risk of catastrophic failure. Since the Heikkilä methodology assigns scores based on intrinsic chemical properties, the maximum penalties for Flammability ($I_{FL} = 4$) and Explosiveness ($I_{EX} = 4$) cannot be directly reduced, as the fundamental nature of hydrogen gas remains unchanged. However, the Minimization actions, specifically coupling the electrolyzer directly to a fuel cell and transitioning from high-pressure gaseous tanks to solid-state metal hydride storage are critical steps taken to maintain the hazard boundary. By eliminating the requirement for hydrogen storage, OSBL lowered its initial score from 2 (assigned for pressurized storage) to 1 or 0, as metal hydrides operate at near-ambient pressure and handle non-explosive solid media.

Furthermore, simplification strategies further reduce the physical hazard scores. By stripping away unnecessary equipment and using standardized stack modules, the safe process structure (I_{ST}) index is reduced from its initial score of 3 to 2 by eliminating complex piping networks and minimizing potential mechanical failure points. For material-related hazards, the substitution of standard steel with titanium nitride-coated plates does not lower the intrinsic Corrosiveness score ($I_{COR} = 2$), but this action is taken to safely maintain structural integrity against the highly acidic internal environment. More importantly, combining robust reinforced ePTFE membranes (Substitution) with active back-pressure regulators that ensure a near-zero pressure gradient ($\Delta P \approx 0$) and optimized channel depths for heat dissipation (Moderation) directly targets the root causes of membrane degradation and thermal accumulation. While the Process Pressure ($I_P = 2$) and Process Temperature ($I_T = 1$) scores are maintained at their optimal operational baselines to preserve system efficiency, these physical controls actively suppress gas crossover.

As a result of implementing inherent safety design, the process inherent safety index (I_{PI}) undergoes a substantial reduction, dropping from its baseline score of 9 to a highly optimized score of 6. On the other hand, while the chemical inherent safety index (I_{CI}) remains intrinsically fixed at 17 due to the immutable properties of hydrogen and oxygen, the

strategic integration of these design improvements yields a quantifiable enhancement in the system's safety profile. This measurable shift effectively lowers the total Inherent Safety Index (I_{TI}) from 26 down to 23.

4.0 CONCLUSION

This study evaluated the inherent safety of a proton exchange membrane water electrolysis (PEMWE) system using the Inherent Safety Index (ISI). The assessment determined that PEMWE is a medium-hazard process, dominated by the immutable chemical risks of hydrogen, specifically its wide flammability range and high explosive energy, while process hazards remained at manageable levels. The Heikkilä method proved highly advantageous for this evaluation due to its simplicity in rapidly screening these risks during the early design phase. To mitigate the identified risks, this study provides targeted recommendations based on Inherently Safer Design (ISD) principles, demonstrating that process-level hazards can be significantly lowered by eliminating pressurized storage and simplifying system pipelines. Despite its practical advantages, the methodology exhibits notable limitations, including a lack of parameter weighting and an inability to index specific electrochemical threats such as electrical hazards. Consequently, to ensure that medium-level hazards are not undervalued, future engineering phases should integrate detailed, probabilistic Quantitative Risk Assessments (QRA) and Hazard and Operability Studies (HAZOP), alongside complementary frameworks like Prototype Index for Inherent Safety (PIIS) or i-Safe. Ultimately, implementing these foundational safety strategies ensures that PEMWE technologies can be safely and sustainably scaled for commercial green hydrogen production.

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