A FRAMEWORK TO ANALYZE THE SAFETY OF HYDROGEN PRODUCTION SYSTEMS

A Thesis

by

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MASTER OF SCIENCE

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ABSTRACT

Determining safety techniques in hydrogen production is important in creating a hydrogen economy. Choosing the safe technology is challenging task given evolving nature of the technology and public expectation of higher safety and sustainability. Additionally, process upsets in such highly hazardous process sensitive operation can cause catastrophic events. Releasing hydrogen is dangerous because of its high combustibility and thermodynamically unsafe properties. Therefore, accounting for root causes and diagnosing the effects of extreme process deviations during the design process is paramount in avoiding disasters.

This thesis consists of two objectives: addressing the hydrogen production decision-making process and creating a diagnosis tool for finding hydrogen production. Using the Multi-Criteria Decision-Making (MCDM) approach, the decision-making process is streamlined towards determining the best suited hydrogen production process. The criterion for this study considers efficiency, safety, and infrastructure and considers qualitative and quantitative parameters of interest.

The second objective is addressed by using a heuristic-based approach and creating the novel Process Risk Index (PRI). This framework integrates the PRI with a risk map to consider possible operating risks. The risk map captures process deviations and is benchmarked with a well-established safety index. Creating this risk identification tool allows decision-makers to revisit the system safety after implementing safety recommendations for deviations.

DEDICATION

To my family and friends who have supported me along the way.

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NOMENCLATURE

MJ	Megajoules
kg	kilogram
GGE	Gasoline Gallon Equivalent
SMR	Steam Methane Reforming
POX	Partial Oxidation
ATR	Autothermal Reforming
AE	Alkaline Electrolysis
PEM	Proton Electrolyte Membrane
SOEC	Solid Oxide Electrolyzer Cell
S-I	Sulfur-iodine
Cu-Cl	Copper-Chlorine
MCDM	Multi-criteria Decision Making
AHP	Analytic Hierarchy Process
FTOPSIS	Fuzzy Technique for Order of Preference by Similarity to Ideal Solution
O&M	Operation and Maintenance
LInX	Life-cycle Index
HAZOP	Hazard and Operability Study
F&EI	Fire and Explosion Index
I2SI	Integrated Inherent Safety Index
HEX	Heat Exchanger
WGS	Water Gas Shift
PSA	Pressure Swing Adsorption

PRI	Process Risk Index
FEDI	Fire and Explosion Damage Index

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1. Introduction and Background

1.1 Project Summary

Hydrogen's high-energy properties must be properly harnessed or otherwise cause potentially fatal consequences. If successful, hydrogen has potential as the fuel of the future. Significant research has increased the amount of available hydrogen production techniques. However, comparing and considering safety when deciding the best suited hydrogen production technologies and operational safety, has often been overlooked. Analyzing hydrogen production technologies through a lens of safety contributes towards a self-sufficient hydrogen economy. This project contains two main objectives:

- To create a framework the comprehensively addresses a best suited process or technology with respect to safety, control, and feasibility.
- To create a flexible risk indexing method that screens for the root causes then allow for appropriate process risk management to implement corrective actions.

This study uses Multi-criteria Decision Making (MCDM) to decide safety, feasible design, and operational conditions in choosing the most suitable hydrogen production technology. The study chooses between six different hydrogen production technologies, categorized into two different types, natural gas and electrolytic. After weighting parameters and calculating the scaling, the input values indicate that steam methane reforming (SMR) is the most suitable hydrogen production method. Uncertainty analysis is used to address uncertainties in the study, although there is no change in the overall results. Sensitivity analysis shows that rank reversal is possible, and results should be closely monitored when highly weighted parameters experience value changes.

After deciding upon the best-suited technology we implement SMR into a model that determines the process's safety. The second portion of this project narrows its focus onto providing a safety metric for the SMR process, creating the Process Risk Index (PRI). The PRI captures deviations and normalizes to a scaled value for comparability. This study analyzes the synergistic effects from upstream operating value changes. A risk map provides an intuitive understanding and visual indicator of the system risk. The results show that the PRI provides a successful diagnosis the synergistic effects from upstream changes. Additionally, the PRI is more sensitive and adaptable to more popular safety indexing methods in operational changes.

The models from this project successfully determines that steam methane reforming (SMR) is the most suitable hydrogen production technology. SMR is integrated into a risk map which detects acceptable and unacceptable risk. The results stemming from using the PRI provides an adaptable model that identifies safe operation. Thus, the PRI is system-specific and can diagnose dangerous units when optimizing operating conditions.

1.2 Background

There is a significant demand for energy carriers and sources. With the US consuming about 90 quadrillion British thermal units, 3 times more than 1950, additional energy methods are explored [3]. Additionally, the carbon dioxide that is emitted from burning fossil fuels and nonrenewable sources contribute towards atmospheric heat trapping and can affect the climate [4]. Lastly, interrupting traditional oil and gas supply chains has adverse economic effects [5]. Finding an energy carrier that is efficient, cost effective, reliable, and environmentally friendly would improve the current energy infrastructure. Although there are a variety of proposed alternative fuels, this thesis focuses on hydrogen as an energy carrier.

Hydrogen has been a sought out energy carrier because of its energy density (120 MJ/kg) compared to gasoline (44 MJ/kg) and liquefied natural gas (49.4 MJ/kg) [1]. In addition to energy density advantages, burning hydrogen does not release carbon emissions. This results in reducing the carbon footprint and reducing the environmental strains. A proposed use of hydrogen is in fuel cells, which offer energy dense power to transportation vehicles and utilizes electrochemical reactions by converting hydrogen into electrical energy and heat [6, 7]. Other works compare the advantages of different types of fuel cells and their respective mechanisms [7, 8].

Although hydrogen is touted for its inherently efficient properties, there are concerns regarding its infrastructure and safety. Currently, there are well-established hydrogen production processes such as steam methane reforming (SMR), but logistical concerns arise regarding transporting and storing hydrogen require specific transportation materials [9]. Additionally, thermodynamic properties are safety concerns. Hydrogen has a low ignition energy (0.017 mJ) as compared to natural gas (0.23 mJ) [10]. Reducing the ignition energies requires more intensive safety protocols. As the smallest element, hydrogen will permeate through or corrode traditional metal containers. Additionally, hydrogen's high flammability range (4-77 vol. %) coupled with its ability to permeate makes combustion a more likely event than other gases [10]. Finally, failing to contain hydrogen leads to high consequence, destructive effects because of its high energy density. There are collaborative efforts, specifically in European countries towards establishing a safer hydrogen economy. The European hydrogen research community has established the hydrogen incident and accident database (HIAD), an open-source database, to encourage and improve collaboration towards hydrogen safety [11]. Further efforts and improvements towards preventing hydrogen-related accidents and establishing a strong safety culture will reduce the risk in hydrogen production.

1.3 Motivation and objectives

1.3.1 Contributions of this study

Serious, comprehensive research investigating hydrogen safety and adjusting for extreme process scenarios are necessary steps to achieve and have hydrogen as a mainstream energy carrier. Multiple efforts and frameworks for implementing a hydrogen economy are proposed [12, 13, 14]. There are different hydrogen production methods; some methods require fossil fuels while others utilize electricity and renewable energy [15]. Deciding upon a method requires intensive amounts of data and a robust, systematic method. Previous studies have used multi-criteria decision making (MCDM) framework towards choosing the best-suited hydrogen production technology [16, 17, 18]. However, these studies primarily focus on the economic and operational aspects and overlook safety. This study builds upon utilizing MCDM and adds comprehensiveness to these studies by incorporating safety. This study then conducts a safety investigation of a given hydrogen technology. While qualitative methods are proposed in finding hazard scenarios, this requires significant time, effort, and detailed information. A better screening method is risk indexing. Creating a risk index profile is advantageous because they are comparable with other results and relatively easier to implement than traditional hazard analysis. Developing an index that fulfills these needs allows both versatility in implementing different processes, identifies root causes of hazardous units upon process deviations, and future risk mitigation designs.

The objectives of this research are of the following:

- To create a framework the comprehensively addresses a best suited process or technology with respect to safety, control, and feasibility.
- To create a flexible risk indexing method that screens for the root causes then allow for appropriate process risk management to implement corrective actions.

1.3.2 Scope and limitations

This research study focuses contributing towards safe and feasible hydrogen production methods. The decision-making model compiles data from 6 different hydrogen production processes within two categories (natural gas and electrolysis). Mentioned previously, there is a high amount of research and focus on hydrogen production. This study focuses on integrating safety into decision-making models for hydrogen production along with implementing safety indicators in the hydrogen infrastructure. However, the methods in this study are applicable to other production processes for safety applications.

This research study utilizes best available data from literature. However, exact design specifications are not available. The decision-making model and risk index profiles are created with literature data or subject-matter experts' opinion. There is an unknown extent of accuracy between given data and true operational conditions. As a result, this work focuses on establishing a well-structured methodology.

1.3.3 Novelties and contributions

The novelties and contributions of this master's thesis are of the following:

- A novel attempt that quantitatively identifies the most appropriate hydrogen production technology in terms of safety, control, and feasibility. This systematic effort is used to identify the most suitable hydrogen production technology throughout its life cycle. The new method integrates the analytic hierarchy process (AHP) for weighting and the life-cycle index approach (LInX) and finds the most appropriate technology. This new model captures the uncertainty of the results along with the parameter sensitivity. This research method is presented in Chapter 2.

- A new method is proposed for screening unsafe conditions from operational process deviations and determining the success of risk minimization strategies. This method uses the steam methane reforming (SMR) hydrogen production process as a case study. This method uses a heuristics-based approach to create a process risk index (PRI). The PRI ensures flexibility and is estimated based on operational parameters (temperature, pressure, flow rate) for each unit in the SMR process. This PRI is translated into a risk map and helps users identify process hazards from operational deviations. The aim of this research is to allow decision-makers a method to propose a risk-minimization strategy after proposing process deviations and identifying hazards. The new strategy's success extent is confirmed through additional risk map iterations. The methodology is presented in Chapter 3.

1.3.4 Thesis Organization

The present thesis is written in the format of manuscripts. The first is a peer-reviewed journal paper. The second is currently under development for journal publication. Details of the thesis organization are highlighted in Figure 1.1. The introduction and conclusion are presented in Chapters 1 and 4, respectively. Chapters 2 and 3 are prepared according to the peer-reviewed journal's submissions.

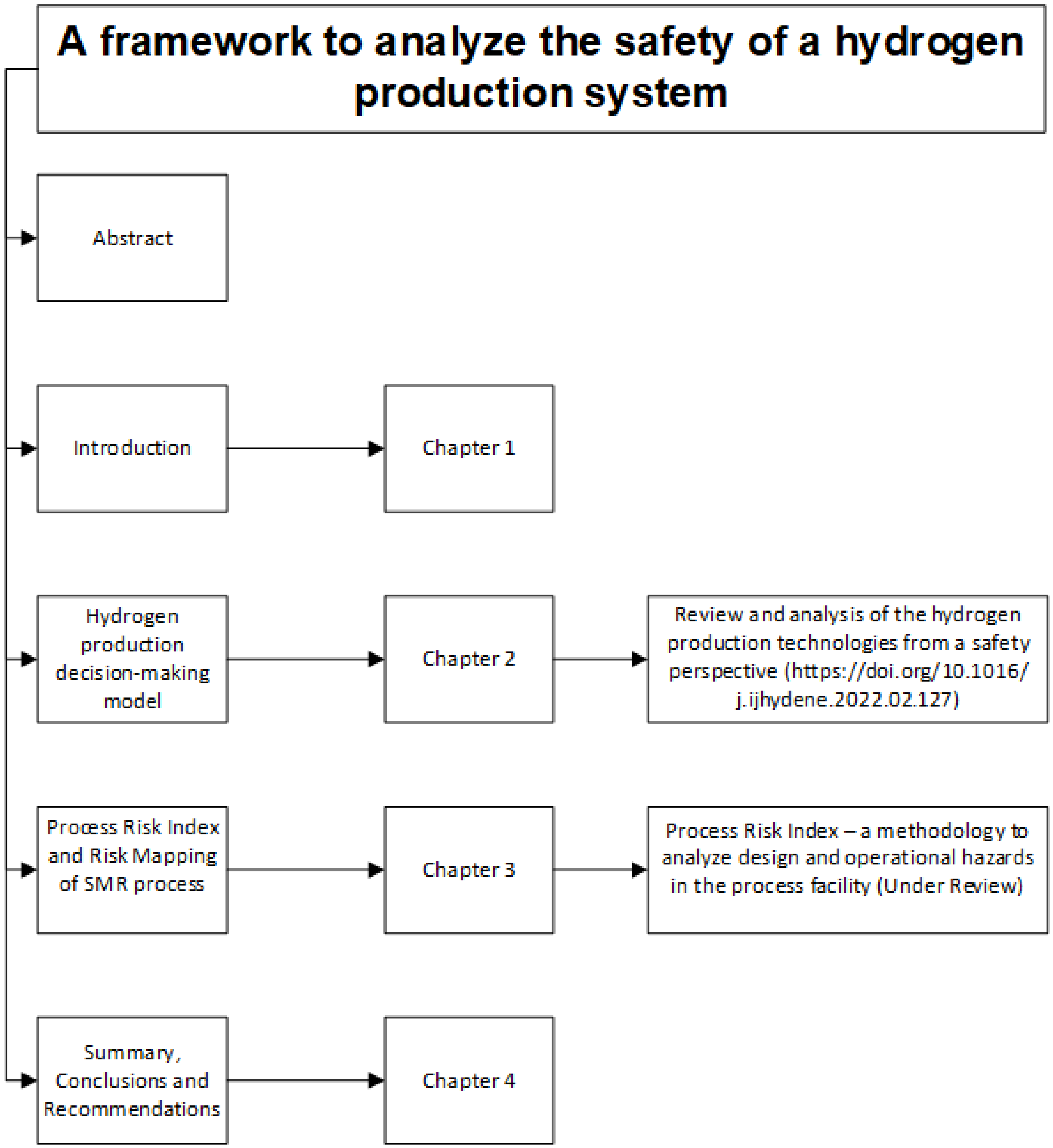

Figure 1.1: The thesis organization and its relevant publications

Chapter 2 reviews and decides upon the best hydrogen production technology. The content of this chapter is published and available online in the journal of *International Journal of Hydrogen Energy 2022; 47(29): 13990.*

Chapter 3 introduces an innovative approach towards creating a flexible risk indexing system. This system can diagnose root causes and identify if corrective actions are effective. The content of this chapter is submitted to the journal of *Process Safety and Environmental Protection.*

2. Review and Analysis of the Hydrogen Production Technologies from a Safety Perspective [1]

by Elsevier

2.1 Introduction

As many countries and governments are pushing for a net zero carbon emission and cleaner energy, hydrogen has emerged as a potential energy carrier and an alternative to fossil fuels due to its high energy density (120 MJ/kg) compared to gasoline (44 MJ/kg) and liquefied natural gas (49.4 MJ/kg) [19, 20]. However, producing hydrogen costs significantly more than producing fossil fuels. The average cost of producing hydrogen is at least five times higher than that of fossil fuels ($16.26/ Gasoline Gallon Equivalent (GGE) versus $3.09/GGE [21]. A common challenge in the storage and transportation of liquid hydrogen is the lack of logistics and appropriate infrastructures. Common storage materials such as steel alloys are not suitable to store liquid hydrogen. The usage of hydrogen as a fuel for mobile and remote applications will require significant research efforts in the development of chemically inert materials with diffusion resistance that can safely and properly store the liquid hydrogen. These effort would involve using underground storage reservoirs to store the hydrogen [9]. However, before hydrogen can be used as a liquid fuel, a proper technology must be selected that has positive economic and environmental impacts. In this study, we investigate the different types of hydrogen production technologies with an emphasis on cost, environmental, efficiency, and safety factors. We discuss both renewable and non-renewable hydrogen production. The specific focus is gray hydrogen, produced through methane reforming, and green hydrogen, produced through a clean and renewable energy sources [22].

[1] Reprinted with permission from "Review and Analysis of the Hydrogen Production Technologies from a Safety Perspective" by Kevin Chau, Abdoulaye Djire, and Faisal Khan, 2022. *International Journal of Hydrogen Energy*, Volume 47, Issue 29, p. 13990-14007

2.1.1 Hydrogen from Natural Gas

2.1.1.1 Steam Methane Reforming

Steam methane reforming (SMR) is a well-established technology that accounts for 50% of the world's total hydrogen production and 95% of the US hydrogen production [23]. Its attractiveness is attributed to its large-scale capabilities and relatively inexpensive production costs. The reforming process (Eq. 2.1) reacts steam with methane to produce hydrogen [24]. Pressure swing adsorption (Eq. 2) utilizes Le Chatelier's principle to convert the by-product carbon monoxide (CO) into hydrogen through water gas shift reaction [25].

$$CH_4 + H_2O \longrightarrow CO + 3H_2, \quad \Delta H_r = 205.9kJ/mol \quad \text{[26]} \tag{2.1}$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \tag{2.2}$$

While SMR is presently the preferred technology for hydrogen production, the main disadvantages of SMR are its energy intensive and high carbon emission.

2.1.1.2 Partial Oxidation Reaction

Another process that is used to produce hydrogen from natural gases is partial oxidation reaction (POX). POX is an attractive exothermic process that reacts hydrocarbons such as methane with oxygen to produce hydrogen (Eq. 2.3) [24]. However, closely monitoring of the temperature is required in the POX process to prevent safety issues such as thermal runaway.

$$CH_4 + \frac{1}{2}O_2 \longrightarrow CO + 2H_2, \quad \Delta H_r = -35.6kJ/mol \quad \text{[26]} \tag{2.3}$$

2.1.1.3 Autothermal Reforming

Autothermal reforming (ATR) combines the principles of both SMR and POX into one unit. This process begins with pure oxygen or oxygen in air to react with methane to form hydrogen. The unreacted methane undergoes the SMR production process in Equation 2.1 by reacting with oxygen and water on a nickel catalyst in a bed reactor. The advantages of using ATR are inexpensive catalyst usage and absence of energy input. Unlike POX which adds steam after oxidation, ATR mixes all three components (CH_4, H_2, and H_2O) in one stage (Eq. 2.4), reducing the number of necessary steps [27].

$$CH_4 + O_2 + 2H_2O \longrightarrow 10H_2 + 4CO, \quad \Delta H_r \approx 0kJ/mol \tag{2.4}$$

2.1.2 Hydrogen from Electrolytic Sources

2.1.2.1 Alkaline Electrolysis

Alkaline electrolysis (AE) is a mature and well-established hydrogen production technology. This requires the splitting of water to form hydrogen. An overall water splitting reaction is shown in Equation 2.5. This process involves an alkaline solution such as KOH or NaOH. A simplified explanation of alkaline electrolysis is that water reduction occurs on the cathode surface (typically nickel) and produces hydrogen gas and two hydroxyl ions. These hydroxyl ions then diffuse through a diaphragm to the anode and become oxidized [28]. Industrial alkaline electrolyzers use nickel-based catalysts because of their availability and cost effectiveness. However, hydrogen production from AE has suffered from a cost and chemical perspective. SMR's production cost is significantly lower than AE. In addition, AE uses highly corrosive chemicals in producing hydrogen, a safety concern.

$$2H_2O \longrightarrow 2H_2 + O_2 \quad \text{[29]} \tag{2.5}$$

2.1.2.2 Proton Electrolyte membrane

Unlike AE systems, proton electrolyte membrane (PEM) electrolysis eliminates the need for highly corrosive electrolytes such as potassium hydroxide. They use polysulfonated membranes as the electrolyte [29]. One significant advantage is operating at higher pressures which, to an extent, reduces the energy required for operation. Other advantages are competitive capabilities in the design and a faster response time than AE [29].

2.1.2.3 Solid Oxide Electrolyzer Cell

Solid oxide electrolyzer cell (SOEC) electrolysis is a relatively new technology that is yet to be commercialized. Instead of using traditional metal catalysts such as nickel, SOEC utilizes conductive ceramics as catalysts. SOEC can operate at higher pressure and temperatures thereby improving the thermodynamic efficiency of the water-splitting reaction [29]. This results in energy savings which lead to lower production costs. However, one of SOEC's drawbacks is it requires highly specialized and expensive materials which have a short lifespan in SOEC operations.

2.1.2.4 Safety Considerations and Technical Aspects

Safety plays a key role in the alkaline and PEM electrolyzes. There are three main steps that must be considered in both technologies: water purification, electrolysis, and separation. Each step requires careful attention because, if neglected, disastrous results can occur. The water treatment unit deionizes and purifies the tap water then removes excess heat using a heat exchanger. The purification unit often is accommodated with an heat exchanger to set an appropriate operating temperature [30]. After water treatment, electrolysis occurs. Alkaline electrolysis has safety concerns because this step involves corrosive chemicals at a 20-30% concentration, and can etch at higher temperatures [31]. PEM avoids bypasses using corrosive chemicals and instead uses a solid and conductive polymeric ion-exchange material. However, the main concerns that is often studied is the effects of cross-permeation and uneven water distribution. Cross-permeation across membranes cause disastrous results because of the flammability mixtures that occur when hydrogen tries to recombine with oxygen. Uneven water distribution leads to the destruction of membrane electrode assemblies and causes gas accumulation inside the stack [32]. Cross-permeation concerns are amplified at higher pressure conditions [28, 33]. Other safety hazards that contribute to potential disastrous results include risks include material defects or deterioration and sensor failure [34]. Therefore, continuous monitoring of process conditions and water distribution are necessary when performing electrolysis.

2.1.3 Hydrogen from Alternative Sources

2.1.3.1 Steam Iron Process

The steam iron process is a highly mature hydrogen production technology. There is no synthesis gas reactant. Two main goals occur in the traditional process. A sufficient amount of iron or wustite must be present to react with steam and produce hydrogen gas shown in Equations 2.6 and 2.7 [35, 36]. The second goal is to use coal and use its emissions (CO) to reduce the iron oxides. Reaction pathways involving reducing iron oxides and hydrogen production must be considered when performing operations.

$$Fe(s) + H_2O \longrightarrow FeO(s) + H_2(g), \Delta_{900^\circ C} = -16.8kJ/mol \tag{2.6}$$

$$3FeO(s) + H_2O(g) \longrightarrow Fe_3O_4(s) + H_2(g), \Delta_{900^\circ C} = -43.2kJ/mol \tag{2.7}$$

The disadvantage of this technology is its lack of efficiency. Since desirable reactions are performed at different temperatures, optimizing the temperature becomes a challenge. Additionally, this process uses primarily coal and oil, but recent research has shifted towards using alternative fuels and natural gas as reducing agents for inherent cleaner emissions [37, 38].

2.1.3.2 Sulfur-iodine (S-I) Cycle

The S-I Cycle is a thermochemical hydrogen production cycle used in water splitting. This cycle is attributed to coupling with nuclear reactors to reduce operation costs and is compared to high temperature electrolysis [39]. This cycle consists of three steps: hydrolysis (Eq. 2.8), oxygen production (Eq. 2.9), and hydrogen production (Eq. 2.10) [40].

$$I_2(l+g) + SSO_2(g) + 2H_2O(g) \longrightarrow 2HI(g) + H_2SO_4(l) \tag{2.8}$$

$$H_2SO_4(g) \longrightarrow SO_2(g) + H_2O(g) + 0.5O_2(g) \tag{2.9}$$

$$2HI(g) \longrightarrow I_2(g) + H_2(g) \tag{2.10}$$

The disadvantage of this cycle is safety because it requires corrosive chemicals and high temperature conditions. Iodine (I2), in addition, is difficult to separate from other gases at high temperatures and has a high sublimation potential. Finding the right equipment to address the challenges associated with I2 requires the right equipment and is an engineering challenge [39].

2.1.3.3 Copper-Chlorine (Cu-Cl) Cycle

Another thermochemical, water-splitting cycle includes the Cu-Cl cycle. There are two main cycles of which are a 5-step and 4-step cycle, of which have different energy requirements. This cycle is attractive because it operates on relatively low voltage, temperatures (530°C), and lower grade heat [40]. Additionally, the cycle will recycle all materials and make hydrogen production more environmentally friendly [41].

4 step cycle: electrochemical (Eq. 2.11), physical (Eq. 2.12), hydrolysis (Eq. 2.13), and thermolysis (Eq. 2.14).

$$2CuCl(aq) + 2HCl(aq) \longrightarrow 2CuCl_2(aq) + H_2(g) \tag{2.11}$$

$$2CuCl_2(aq) \longrightarrow 2CuCl_2(s) \tag{2.12}$$

$$2CuCl_2(s) + H_2O(g) \rightleftharpoons Cu_2OCl_2(s) + 2HCl(g) \tag{2.13}$$

$$Cu_2OCl_2(s) \longrightarrow 2CuCl(l) + 1/2O_2(g) \tag{2.14}$$

One notable safety concern and disadvantage of the Cu-Cl cycle is the corrosive chemicals involved [41]. A more pressing challenge is optimizing and integrating the electrolytic design [42].

2.1.3.4 Nuclear hydrogen technologies

Nuclear fission is a proposed thermochemical process for hydrogen production and is highly efficient, which lowers the cost of electricity. France uses nuclear power for up to 78% of its electricity. This allows for a low electricity cost and has made the country one of the largest net exporter of electricity in the world [43]. With high efficiency and low cost, nuclear power is proposed as a potential energy source for high-temperature electrolytic processes and S-I and Cu-Cl cycles [39, 44, 45]. However, although nuclear energy is economically attractive, its main concern is safety when failure occurs [45]. Past and potential consequences of reactor failure cause concerns with regards to physical, environmental, and psychological impact [46, 47].

2.1.4 MCDM and Research Gaps

The number of options available with different features and capabilities does not allow a straightforward decision. Multi-criteria decision-making (MCDM) is capable of guiding decision making. The Analytic Hierarchy Process (AHP) is a MCDM technique that quantitatively compares different criteria and provides a point value final decision [48]. AHP is versatile and can apply its weighting scheme to different types of problem, of which include areas such as microalgae [49], power [50], chemicals [51], and other problem statements. One drawback from using AHP is the uncertainty in the literature data reported by different groups. Previous studies have compared hydrogen production technologies with an emphasis on the economic benefit using the MCDM approaches [16, 17, 18]. Thengane et al. evaluate the alternatives and attractiveness of eight different hydrogen production technologies using a cost-benefit analysis. The criteria include greenhouse gas emissions, raw material and utilities consumption, energy efficiency, scalability, waste disposal and atmospheric emissions. The findings emphasize the importance of expert opinion in the weighting scheme which affects the role in AHP and creates changes in the rank. The study utilizes quantitative criteria and uses a cost-benefit curve in terms of overall benefit with respect to the annual technological cost [16]. Although quite comprehensive, this study does not consider the effect of technological innovations such as automation. AHP can be combined with other techniques. Xu et al. demonstrates this and combines fuzzy AHP with FTOPSIS and DEA to find the most desirable hydrogen production technology in Pakistan. The criteria focus on cost parameters which include capital cost, feedstock cost, O&M cost, hydrogen production, and CO2 emission. The proposed alternatives include biological, thermochemical, electrolysis, and solar water splitting hydrogen production technologies. The study concluded that clean energy technologies of PV electrolysis, wind power electrolysis, and biomass gasification were the ideal hydrogen technologies for Pakistan [17]. This study highlights different aspects such as scalability social acceptance but does not consider the risk of failure.

2.1.5 Motivation of Current Work

Overall, while MCDM and AHP studies mentioned are quite comprehensive, there is no known work that simultaneously addresses the safety, life-cycle, and environmental impacts of the different type of hydrogen technologies. This work addresses this knowledge gap by creating a decision-making tool beyond a purely economic and environmental standpoint. Especially, this study incorporates the design, execution, and safety aspects when comparing different hydrogen production technologies, which is something that prior work overlooked. The technologies studied include: SMR, ATR, POX, AE, PEM, and SOEC. We use combine AHP with life-cycle index (LInX) assessment approaches to find the most desirable hydrogen technology based on safety and environmental impacts. The addition of the LInX system addresses the problems through a given technology's life cycle [52]. Integrating this approach creates a standardized application towards all the hydrogen technologies that were discussed above. This is an important study as safety failure in hydrogen production plants can cause catastrophic effects and major economical downfall [53]. The risk-based analysis approach taken in this study addresses these issues by factoring process controllability, safety, and automation into the decision-making process. Here, we adopt techniques from both AHP and LInX using composite programming and quantitatively compare the different hydrogen production technologies discussed above. Given the range of data, we use fuzzy numbers to capture the uncertainty because AHP does not capture uncertainty. We address criteria necessary towards the success of products' health, safety, and cost. The work conducted here expands upon the LInX technique, which accounts for both controllability and design parameters. We parameterize the effects of each category to evaluate the importance of each criterion that is made as highly weighted criteria can cause rank reversal if such values have notable changes. We address and highlight the uncertainties in the data by giving ranges to the input data. We also include sensitivity analysis to document the effects of changing parameters on the overall index upon hypothetical changes.

2.2 Research Methodology

2.2.1 Designing the Model

Three main categories are considered in finding the best technology: design, operation, and control. There are various levels to these categories and input parameters including 4 design, 15 operation, and 2 control parameters, highlighted in Figure 2.1 LInX evaluates the life-cycle of the technologies in terms of houses contributing to the overall index [52]. The relationship between different parameters in the roof and room model (Figure 2.2) in LInX requires a synergetic relationship that is considered when modeling the problem. Choosing the associated parameters require a comprehensive coverage with minimal overlap. The study focuses primarily on the inherent design and the implementation of the technologies; although, other factors such as sustainability or social perception can be included.

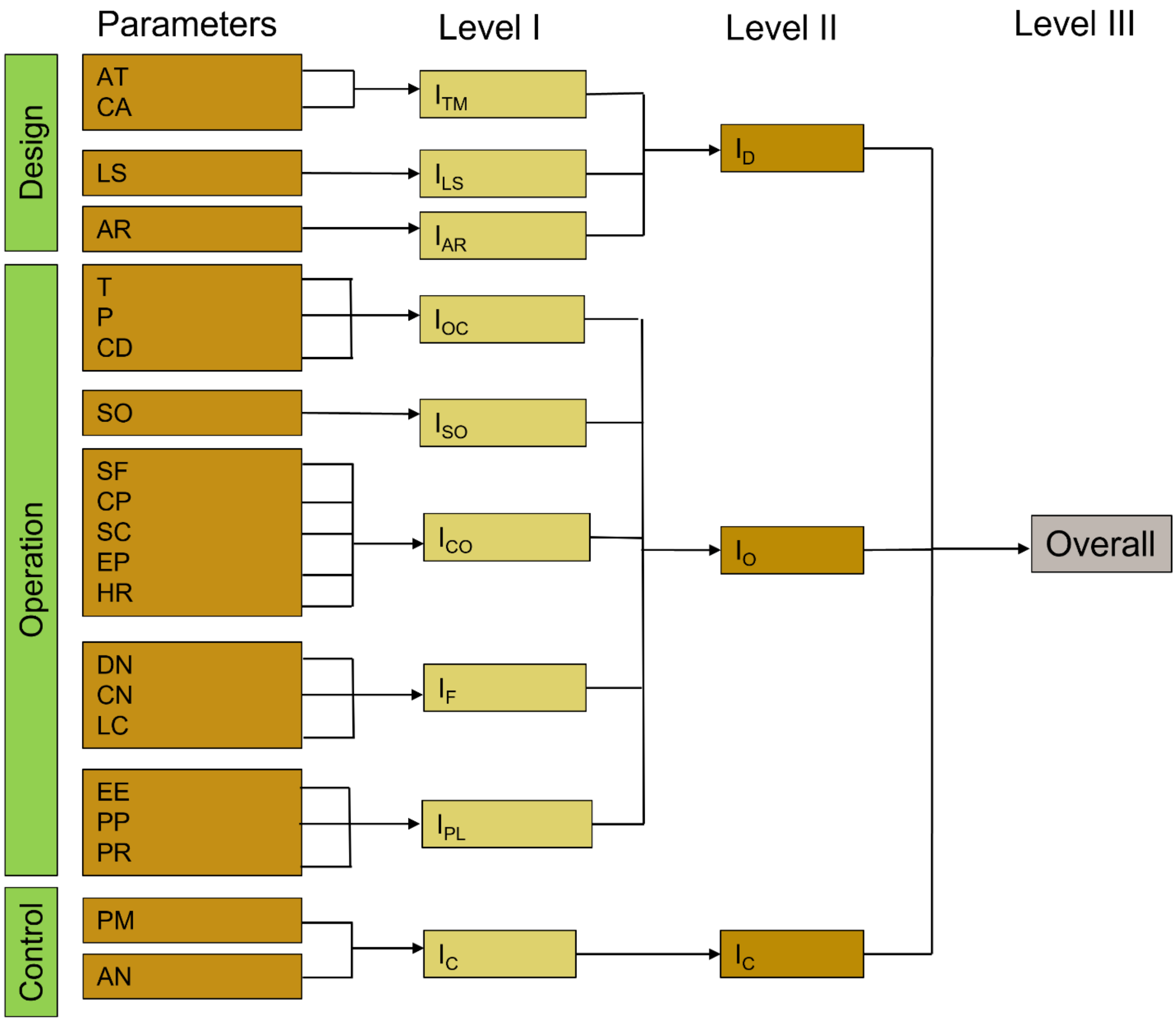

Figure 2.1: Breakdown of the design in choosing the right hydrogen production technology. Abbreviations of parameters are as followed: Age of Technology (AT), Commercial Availability (CA), Longevity of System (LS), Availability of Resources (AR), Temperature (T), Pressure (P), Current Density (CD), Safety of Operation (SO), Soot Formation (SF), Catalyst Poisoning (CP), Stack Compromised (SC), Extra Pressurization (EP), Heating Requirement (HR), Degradation (DN), Corrosion (CN), Levelized Cost (LC), Energy efficiency (EE), Product purity (PP), Production rate (PR), Process monitoring (PM), Automation (AN). Indices are as followed: Technological Maturity (ITM), Longevity of system (ILS), Availability of resource (IAR), Operating Conditions (IOC), Safety of Operation (ISO), Complexity of Operation (ICO), Feasibility (IF), Production level (IPL), Control (IC), Design (ID), Operation (IO), and Control (IC). "Reprinted from Review and Analysis of the Hydrogen Production Technologies from a Safety Perspective [1]"

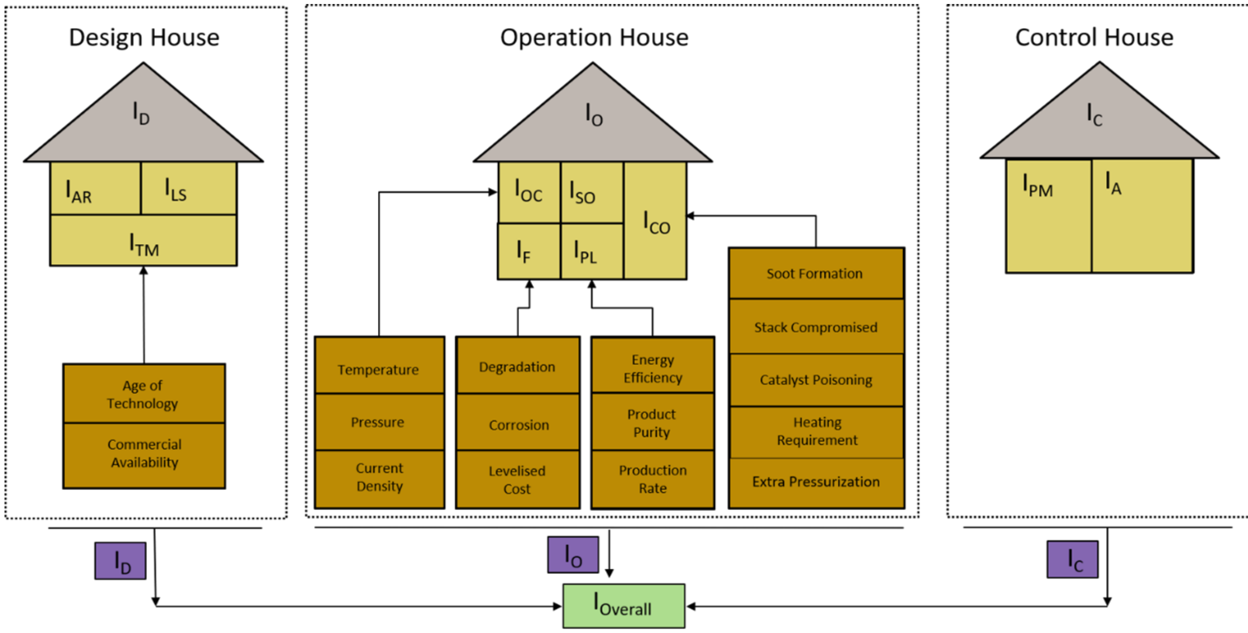

Figure 2.2: Framework of the hydrogen production system. The roofs are the Design, Operation, and Control parameters, and are supported by their respective units. These houses in the framework synergistically work together to give the overall index which reflects the relative attractiveness of a technology. "Reprinted from Review and Analysis of the Hydrogen Production Technologies from a Safety Perspective [1]"

The LInX model used a scale and normalized parameters and contains values between 0 and 1. Decision makers' discretion in scale making was used in cases that involve insufficient data or qualitative parameters. The panels in Figure 2.3(a-i) were derived from comparing possible ranges of each parameter and Table 2.1 was scaled using the linguistic interpretation.

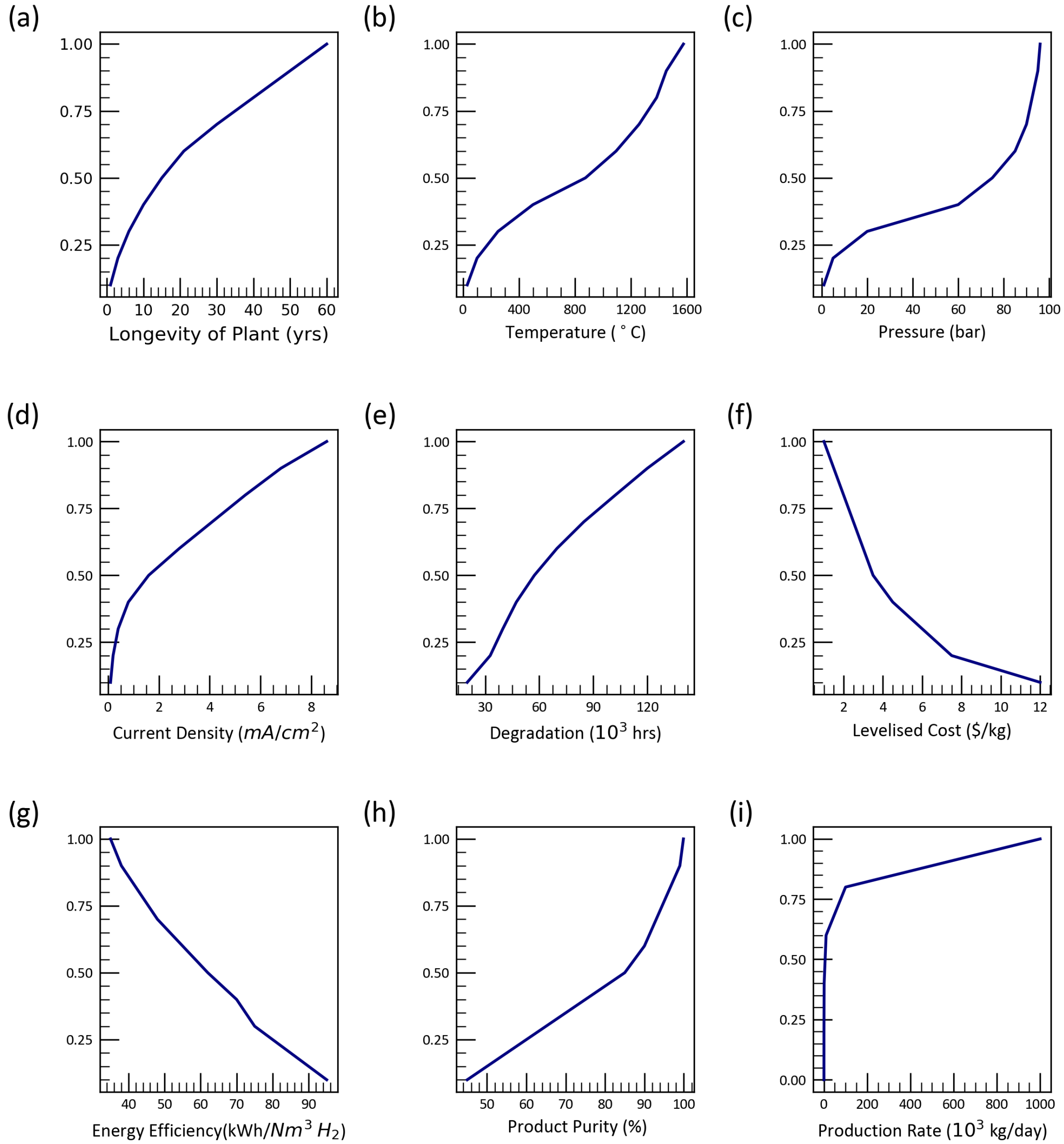

Figure 2.3: Scale for both benefit and cost parameters. (a) Longevity of system. (b) Temperature. (c) Pressure. (d) Current density. (e) Degradation. (f) Levelized cost. (g) Energy Efficiency. (h) Product Purity. (i) Production rate. Note that Levelized Cost and Energy efficiency decrease as their values get larger. Scaled levels rather than actual values were used to allow for greater parameter change flexibility. "Reprinted from Review and Analysis of the Hydrogen Production Technologies from a Safety Perspective[1]"

2.2.2 Design

The design index (D) highlighted the overall concept of the technology design using the following indices: technological maturity, longevity, and availability of resources.

2.2.2.1 Technological Maturity

The age of technology (AT) indicated the amount of time the respective hydrogen production technology was discovered. The scale was made in ranges of time ranging from a fully mature, centuries old technology to a newly discovered, unestablished but promising technology. The commercial availability (CA) binary parameter aided in understanding a given technology's maturity. For example, a CA value of 1 indicates a technology that is commercially available.

2.2.2.2 Longevity of System

The longevity of the system (LS) featured how long the entire plant would operate, if created. Figure 3a utilized logarithmic behavior because efficiency and outdated technology lags in benefit as newer plants arise and surpass these older plants.

2.2.2.3 Availability of Resources

Availability of resources (AR) was scaled qualitatively in Table 2.1 by describing the number of resources available for both the feedstock and the materials necessary to perform the reaction. For example, nickel catalysts in SMR are more plentiful than yttrium stabilized zirconia electrolyte materials in SOEC. Widely available resources yielded higher values on the scale.

2.2.3 Operation

The operation index (O) was calculated by combining the production level index, feasibility index, complexity of operation index, safety of operation index, and operating conditions index.

2.2.3.1 Operating Conditions

Operating conditions referred to the physical process conditions that helped understand the cost and benefits of the technology at hand. Economies of scale accounted for diminishing returns at higher ranges.

Temperature (T) scale corresponded to the increase in the scale value in Figure 2.3b. AE and PEM technologies have notably lower temperature capabilities (30 to 80°C) compared to natural gas technologies which could have temperatures up to 1500°C [54]. A higher temperature in electrolysis correlates with higher efficiency because it reduces the electricity requirement, which is one of the advantages of high temperature-based technologies such as SOEC [55]. However, for natural gas technologies, the opposite occurs, such that lower temperatures contribute toward higher soot content, which could lead to safety concerns.

Pressure (P) was considered beneficial at higher values in Figure 2.3c because of the reduced energy requirement to pressurize the product and aided in efficient storage processes. In addition, a higher pressure of hydrogen in electrolysis improves to a certain extent the energy efficiency [56]. The third component in this category is current density (CD). An electrolytic technology containing a higher current density (CD) requires less volume without compromising product and reduces capital expenditures. Higher current density reduces stack longevity, thereby one must choose how important a smaller volume is at the expense of longevity (Figure 2.3d).

2.2.3.2 Complexity of Operation

The complexity of operation index provided information about what additional inputs or potential negative phenomena occurred during the operation. This index consisted of binary variables which depended on whether the technology exhibited the behavior of interest.

Soot formation (SF) is a common concern in reforming reactions. Incomplete combustion causes carbon deposits, known as soot, to adhere to catalysts or reactor walls. Soot on catalyst surfaces result in catalyst poisoning [57] and leads to complications such as equipment overpressurization and fouling [58]. The catalyst poisoning (CP) parameter extended toward any possibility of poisoning. For example, soot formation ruins the nickel catalyst in SMR [58] or sulfur traces reduces SOEC electrolysis's fuel electrode efficiency [59]. Additionally, ionic compounds such Iron (III) could ruin the PEM electrolytic cell [60].

Stack Compromised (SC) addressed the possibility of a stack losing effectiveness from degradation or poisoning which resulted in reduced efficiency. Since stacks cannot avoid such a phenomenon, all electrolytic technologies exhibited this effect.

Extra pressurization (EP) was considered if a significant amount of pressurization from the very beginning was required for the product. The threshold for meeting this pressurization requirement was above 30 bars which was well above atmospheric pressure, although hydrogen tanks store hydrogen at significantly higher pressures.

Heating requirement (HR) questioned whether technologies required an external temperature input. Exothermic reactions such as POX would not require an energy input but rather commence a reaction to begin heating. Removing heating made the technology more desirable.

2.2.3.3 Safety of Operation

The safety of operation (SO) was simplified due to the nonuniformity in different materials that were present. Due to the unavailability of specific accident data, the rating was subjective and estimated according to Table 2.1 which gave a scale and rated the values of safety.

2.2.3.4 Feasibility

Feasibility consisted of degradation, corrosion, and levelized cost. Corrosion was a binary parameter and therefore only degradation and levelized cost had scales in Figures 2.3e and 2.3f, respectively.

Degradation (DN) of the stack in electrolysis was considered as the average lifetime rather than degradation rate because degradation rate varies due to the multitude of different materials and operating conditions [61]. The scale was maxed at 30 years in electrolysis because electrolysis plants are usually made to last up to 30 years and replacing the stack twice (140K hours equals 16 years of continuous operation) would fulfill such requirements.

Corrosion (CN) was a binary parameter which was a cost function. Therefore, values with 0 meant that corrosivity was possible and was detrimental to the technology. Corrosivity referred to both pipelines and electrode materials.

Levelized Cost (LC) was defined as the cost of production output of hydrogen divided by the overall lifetime. This value created a normalized cost for $/kg of hydrogen. An exponential decay relationship existed because as prices increase at the higher end of the scale, the sensitivity to such price changes affected the scale more than that of an already expensive technology.

2.2.3.5 Production Level

All three sub-criteria in production level utilized economies of scale and therefore had a non-linear scale.

Energy efficiency (EE) was expressed in terms of kWh/kg H_2 as shown in Figure 2.3g. From this, the amount of energy expended was determined. A lower EE value meant higher efficiency because of a lower energy input requirement.

Product purity (PP) occurs after all manufacturing and synthesis processes were completed. The product purity was usually high and resulted at a high starting point. Fuel cells require ultra-pure hydrogen to prevent poisoning [25, 60]. Incremental increases in purity at ultrapure levels yield substantial benefits (Figure 2.3h).

The production rate (PR) was scaled in terms of kg/day in Figure 2.3i to simulate the overall output necessary to meet expectations for hydrogen production. The discrepancies between a prototype such as SOEC versus an established infrastructure like SMR warranted a logarithmic scale.

2.2.4 Control

Control (C) consisted of process monitoring and automation, both of which had qualitative definitions in Table 2.1. A strong control score meant fewer conditions that operators needed to simultaneously monitor. Less monitoring reduced the probability of human error.

Process monitoring (PM) was scaled according to how well the reactions were understood. The lack of understanding of the mechanisms or how operation parameters can be controlled resulted in a lower control index score.

Automation (AN) was scaled in levels ranging from fully automated to fully manual operation. Values were given according to the amount of necessary human interaction needed to perform the hydrogen production process.

2.2.5 Weighting Scheme

Not all indices and parameters in the respective houses, rooms, and units had the same importance to the decision makers. Accordingly, the four subject matter experts assigned the relative importance between each room by making pairwise comparisons between each category. Saaty's AHP method calculated the relative weights for each category [48, 62]. Due to the possibility of inconsistencies, a consistency ratio was calculated from eigenvalues from the respective matrix. Containing this ratio within an order of complete inconsistency (100%) is important in mitigating bias when creating comparisons. As a result, this ratio was ensured to be kept under 10%. Table 2.2 shows the weighting results and all calculations are available upon request.

Table 2.1: Scaling for age of technology, availability of resource, and safety of operation. "Reprinted from Review and Analysis of the Hydrogen Production Technologies from a Safety Perspective[1]"

Scale	**Age of Technology**	**Availability of Resource**	**Safety of Operation**	**Process Monitoring**	**Automation**
0.1	Newly Developed	Extremely Rare and Not Commonly Used (Never been used)	Extremely High with Devastating effects (Nuclear)	Catalytic reactions, mechanisms; "black-box" like; parameters unclear to control	Fully manual
0.2	10 years	Rare but Used (tested one time in 100 years)	Very Highly		Almost fully manual
0.3	25 years	Quite Rare and Not Commonly Used (used more than one and less than 10 in 100 years)	Very High (potential runaway; autocatalytic; explosion)		Mostly manual

Table 2.1 (continued)

Scale	**Age of Technology**	**Availability of Resource**	**Safety of Operation**	**Process Monitoring**	**Automation**
0.4	40 years	Quite Rare and Used (used more than 10 but less than 100 times in 100 years)	High (potential runaway; autocatalytic; explosion)	Very new technology whose conditions and mechanisms are not well understood	More than half manual
0.5	50 years	Slightly Rare but Not Commonly Used (used one in year or one in the region)	Moderately High (pressure; corrosive behavior)		Half manual, half automated
0.6	60 years	Slightly Rare and Used (used more than one in year and one in the year though less than 10)	Moderate	Relatively new technology with continuous studying ideal ratios/conditions	More than half automated
0.7	70 years	Common but Not Commonly Used (used more than 10 times in year and region but less than 100)	Slightly		Mostly automated
0.8	80 years	Common and Abundantly Used (used more than 100 times in year and region)	Slightly Low	Well-defined standards/ parameters to look for in optimization and safety	
0.9	100 years	Extremely Common but Not Commonly Used (used more than 1000 times in year and region; most preferred technology; however, not every use it)	Common		Almost fully automated

Table 2.1 (continued)

Scale	**Age of Technology**	**Availability of Resource**	**Safety of Operation**	**Process Monitoring**	**Automation**
1	100+ years	Extremely Common and Abundantly Used (used by most industries or operation)	Safe/ Minimal consequence (low temperature, pressure, minimal human operation, or maintenance)	Highly controlled, monitored, physical observation	Fully automated

Table 2.2: Weighting results for all criteria. Same colored boxes indicate that sub-sub criteria correspond to the sub-criteria. "Reprinted from Review and Analysis of the Hydrogen Production Technologies from a Safety Perspective[1]"

Main Criteria	**Main Criteria Weights**		**Sub-criteria**	**Sub-Criteria Weight**		**Sub-sub Criteria**	**Sub-sub Criteria Weights**
Design	0.579		Technological Maturity	0.196		Age of Technology	0.2
						Commercial Availability	0.8
			Longevity of System	0.069			
			Availability of Resource	0.735			
Operation	0.187		Operating Conditions	0.063		Temperature	0.312
						Pressure	0.49
						Current Density	0.198
			Safety of Operation	0.389			
			Complexity of Operation	0.121		Soot Formation	0.123
						Catalyst Poisoning	0.16
						Stack Compromised	0.185
						Extra Pressurization	0.359
						Heating Requirement	0.174
			Feasibility	0.272		Degradation	0.137
						Corrosion	0.238
						Levelized Cost	0.624
			Production Level	0.155		Energy Efficiency	0.102
						Product Purity	0.366
						Production Rate	0.532
Control	0.234		Process Monitoring	0.333			
			Automation	0.667			

2.3 Results

Figure 2.4 shows the results for the AHP analysis and Table 2.3 shows the input parameter values for the case study. Although SMR appears to be the best suited hydrogen production technology driven by design and control, there is only a 0.009 difference between SMR and ATR. Due to a range of possible parameter values which causes uncertainties in the data, sensitivity analysis calculations and Fuzzy AHP are performed and are discussed in the Sensitivity Analysis section to test model robustness. Furthermore, the results show that the design index is the largest contributor towards the overall index.

We found using the AHP-LInX hybrid model that SMR in Figure 2.4 was the best suited hydrogen production technology. The results showed that design and control were the biggest factors in this decision.

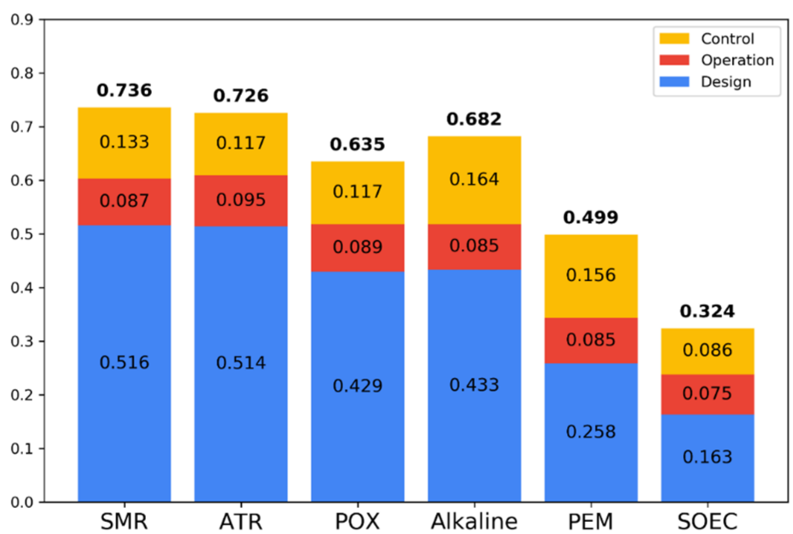

Figure 2.4: The stacked bar chart displays the individual contributions of each index with the bolded topmost value as the total sum of the individual indices (control, operation, design). This case study shows that SMR is the most favorable hydrogen production technology. "Reprinted from Review and Analysis of the Hydrogen Production Technologies from a Safety Perspective[1]"

Table 2.3: Input parameter values for AHP analysis for the different technologies. "Reprinted from Review and Analysis of the Hydrogen Production Technologies from a Safety Perspective [1]"

	SMR	**ATR**	**POX**	**Alkaline**	**PEM**	**SOEC**
Age of Technology	0.8 [63]	.7 [64]	.7[2]	.9 [65]	.7	.5 [29]
Commercial Availability	1	1 [66]	1	1 [29]	1 [29]	0
Longevity of System[3]	0.6	0.6	0.6	0.6	0.6	0.6
Availability of Resource	0.9	0.9	0.7[4] [67, 68]	0.7[5]	0.3[6]	0.3[7] [29]
Temperature	0.5 [69, 70]	0.6 [66, 67]	0.8 [66, 71]	0.1 [29]	0.1 [28]	0.5 [72]
Pressure	0.3 [69]	0.3 [68, 71]	0.3 [68, 71]	0.3 [28, 73]	0.3 [73]	0.2 [74]
Current Density	0	0	0	0.2 [75]	0.5 [29, 76]	0.4 [72, 77, 78]
Soot Formation	1	1	1	0	0	0
Catalyst Poisoning	0 [70]	0	1 [67, 68]	0	0 [60]	0 [59]
Stack Compromised	1	1	1	0	0	0
Extra Pressurization[8]	1 [69]	1 [68, 71]	1 [54]	0	1	0 [74]
Heating Requirement	0	1 [79]	1	1	1	0

[2]POX time of discovery assumed to be around same time as that of ATR
[3]All systems and plants assumed to last for about 25 years to be commercially viable
[4]Assumed as less plentiful due to oxygen gas need
[5]Assumed as less plentiful since high purity water is less plentiful
[6]Stack materials for PEM are rare
[7]Yttrium and zirconium are quite rare non-noble materials
[8]Must meet a threshold of 40 bar

Table 2.3 (continued)

	SMR	**ATR**	**POX**	**Alkaline**	**PEM**	**SOEC**
Safety of Operation	0.3[9] [79]	0.4[10] [66, 80]	0.3 [79]	0.6[11]	0.5[12]	0.6[13]
Degradation	0	0	0	0.6 [76]	0.3 [29, 76, 81]	0.1 [65]
Corrosion	0	0	0	0 [82, 83, 84]	0 [85]	0 [86]
Energy Efficiency	0.5 [87, 88, 89]	0.5	0.5	0.5 [90]	0.7 [91, 92]	0.8 [93]
Product Purity	1 [94]	1 [54]	1[95]	1[82]	1[28, 29, 82]	1 [96]
Production Rate[14]	0.8 [97]	0.4	0.4 [95]	0.4	0.4	0.1
Process Monitoring	0.7 [67]	0.5[15] [67]	0.5	0.7	0.6 [28]	0.3[16]
Automation	0.5 [98]	0.5	0.5	0.7 [99]	0.7 [100]	0.4
Levelized Cost	0.7 [94, 101, 102]	0.8 [94, 103]	0.7 [95]	0.4 [97, 104, 105, 106]	0.4[17][81, 107]	0.4[18] [93]

2.4 Sensitivity Analysis

Data uncertainties are common and necessary to address. To account for uncertainties in the data, we calculated the index uncertainty. The input values were given a lower and upper bound then calculated in the same manner as the index point value calculation. Literature data readily available represented these bounds. Qualitative interpretations were given a Triangular Fuzzy Number [108]. The overall results (Figure 2.5) remained unchanged with the technologies' lower, median, and upper range having the same respective rank. SMR and ATR technologies remained

[9] The possibility of vapor cloud explosions makes SMR more risky

[10] A shorter start up and stop times makes ATR safer, but there is still a risk of vapor cloud explosion

[11] Alkaline electrolysis's relative simplicity makes it less susceptible to explosion

[12] Higher pressure operation in PEM makes operation more dangerous than alkaline electrolysis

[13] SOEC electrolysis's less dangerous chemicals and fewer parts makes it slightly less risky, but higher temperature operation subtracts from safety

[14] All smaller scale technologies are assumed to have a production rate of 50,000 kg/day production rate except for SOEC because it is not yet commercially available

[15] Hotspots can make the process less ideal in terms of efficiency, yield, and control

[16] Relatively new technology that is not well understood and not commercially available

[17] Levelized cost value was calculated from the DOE spreadsheet

[18] Levelized cost value was calculated from the DOE spreadsheet

the most robust within a ±0.100 range.

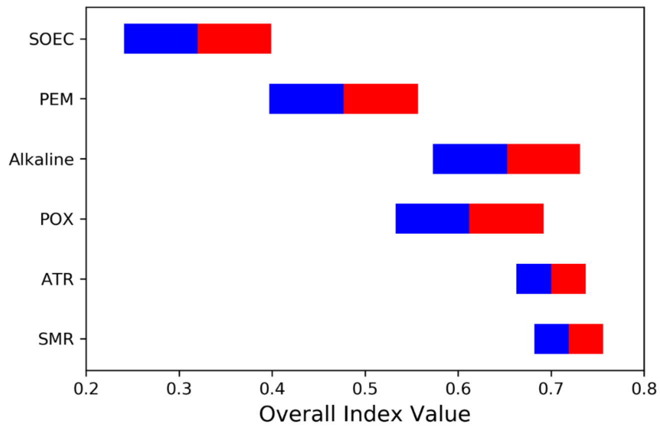

Figure 2.5: Results for uncertainty analysis using fuzzy numbers for the different technologies. The lowest boundary is the left end of the left bar, the median is the interface between the two different colored bars, and the highest boundary is the right end of the right bar. "Reprinted from Review and Analysis of the Hydrogen Production Technologies from a Safety Perspective [1]"

Figures 2.6 to 2.10 show the results of sensitivity analysis for eleven parameters. Percentage change calculations of the parameter's scaled value were made and compared to the parameter change's impact on the category and the risk index. Percentage change values were rounded to the nearest integer. Binary parameters (Commercial availability and Catalyst Poisoning) were modified according to the technology. SOEC, when assumed to have commercially availability, displayed a 28% change in its Index value from 0.324 to 0.415 and a 56% change in the Design category value from 0.163 to 0.254. Catalyst Poisoning was also changed to assume that catalysts were no longer poisoned. All values except POX were assumed to not lead to catalyst poisoning, resulting in an increase in index values. The result showed a 1% change (SOEC and PEM) in the overall index and up to a 4% change (Alkaline) change in the operation category.

The resource availability explored the effects of decreased availability due to situations such as supply chain disruptions. This parameter showed a notable decrease in both the overall index value and the design index (Figure 2.6). An 80% decrease in this parameter could cause up to a 42% decrease in the overall index (SMR and ATR) and up to a 60% decrease in the design index

(ATR). Note that the largest overall index decrease pertained to SMR and ATR while the largest design index decrease referred to SOEC. In addition to the largest percent decrease, the smallest percent decrease in the overall index and design category were 20% and 40%, both belonging to PEM electrolysis.

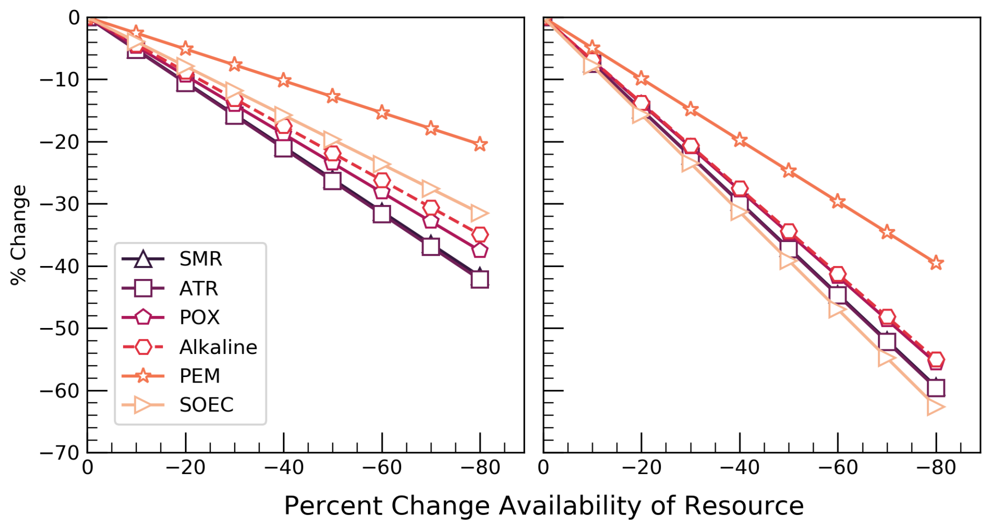

Figure 2.6: Sensitivity analysis results for availability of resource percentage change of overall index (left) and design index (right) for the different technologies. "Reprinted from Review and Analysis of the Hydrogen Production Technologies from a Safety Perspective [1]"

The levelized cost (Figure 2.7) showed the index as quite insensitive to change with a larger effect on operation. The maximal decreases to the overall index belonged to both ATR and SOEC with 4%, respectively for a 100% decrease in the levelized cost parameter with an operation index decrease to ATR of 29%. The minimal decrease effect in the overall index belonged to PEM with 2% and with an operation index decrease of 15% having a tie with Alkaline and PEM.

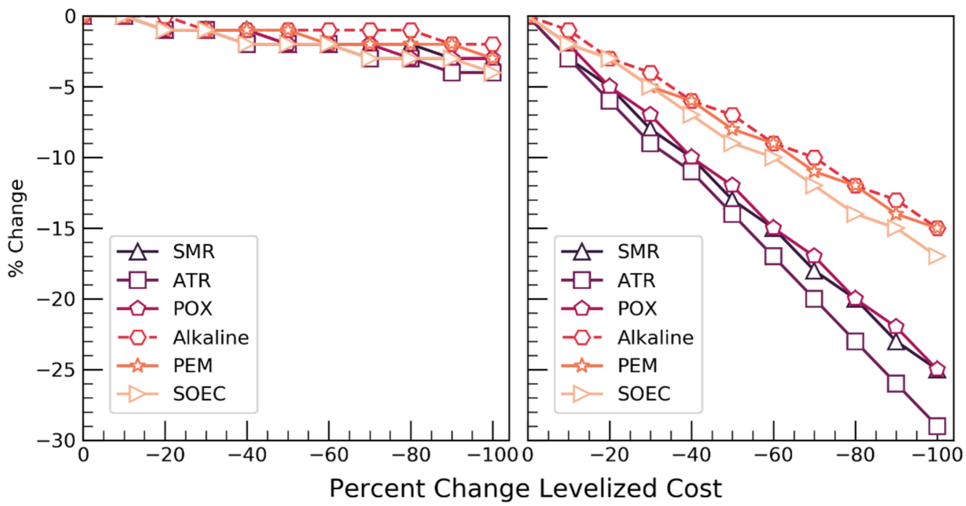

Figure 2.7: Sensitivity analysis results for levelized cost percentage change of overall index (left) and operation index (right) for the different technologies. "Reprinted from Review and Analysis of the Hydrogen Production Technologies from a Safety Perspective [1]"

The energy efficiency parameter 2.8a was highly insensitive to the overall and operation index. Production rate 2.8b was likewise insensitive to the overall index, and it had notable changes of up to a 14% decrease in the operation index.

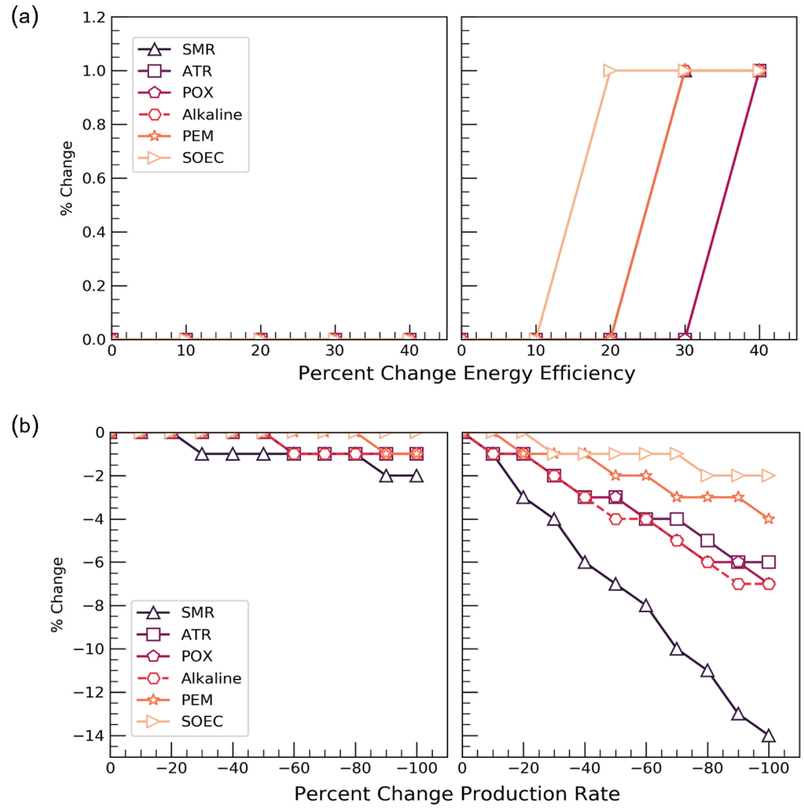

Figure 2.8: Sensitivity analysis results for percentage change of overall index (left) and corresponding index (right) for (a) Energy efficiency and (b) Production Rate. "Reprinted from Review and Analysis of the Hydrogen Production Technologies from a Safety Perspective [1]"

Degradation of all three electrolytic technologies shown in 2.9a did not influence the overall index and changes in the operation index. Technologies were insensitive or exhibited minimal sensitivity toward the current density (2.9b). Safety in Figure 2.9c showed a larger contribution to overall index with SOEC having the largest change of 9% and 40% in the overall and operation index, respectively, corresponding to a 70% increase in the safety parameter. It should be noted that different technologies behave differently in terms of change. For example, SMR and POX both had a 2% and a 15% increase as compared to SOEC having a 9% and 40% increase in the overall index and operation index, respectively.

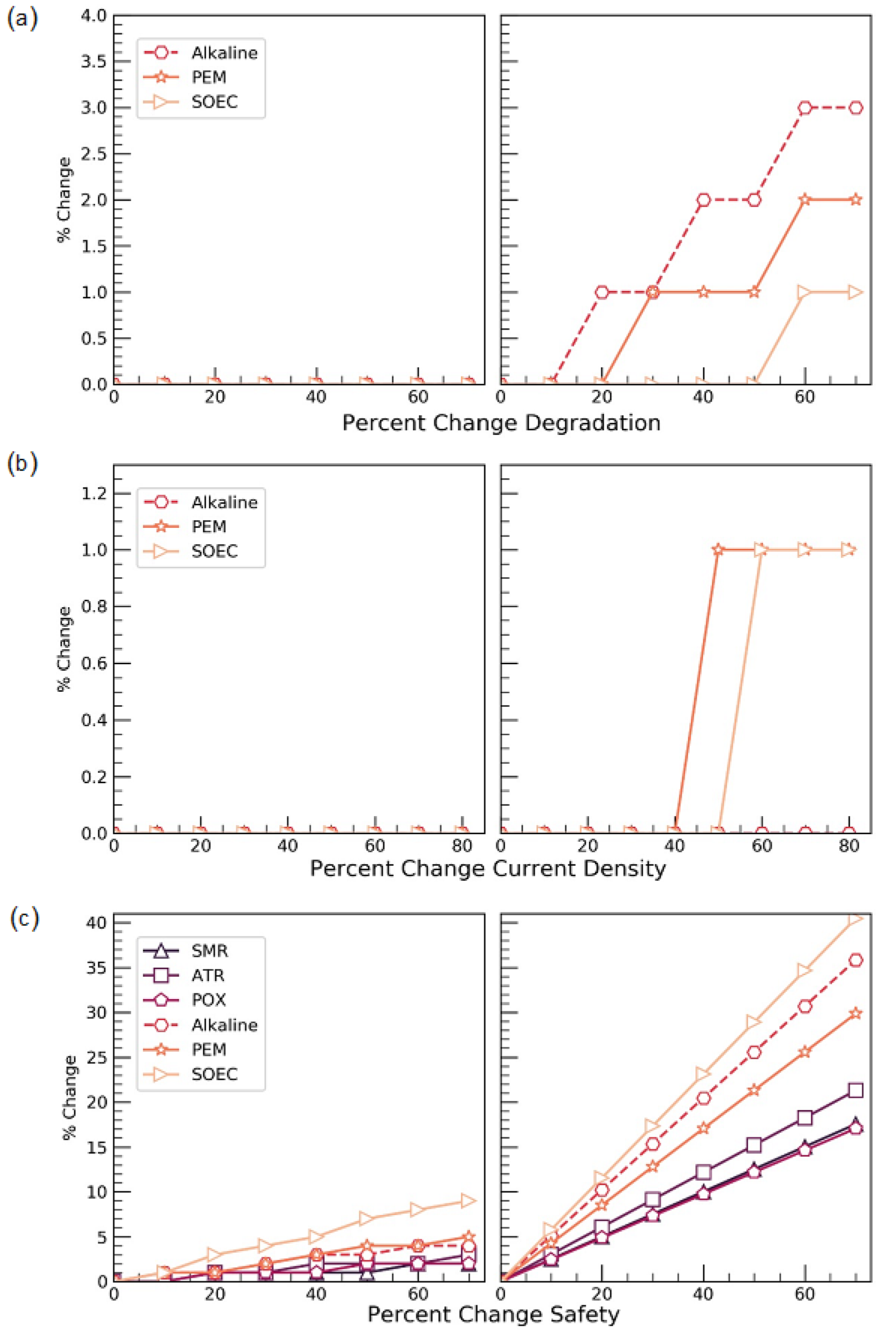

Figure 2.9: Sensitivity analysis results for percentage change of overall index (left) and corresponding index (right) for (a) Degradation, (b) Current Density, and (c) Safety for the different technologies. "Reprinted from Review and Analysis of the Hydrogen Production Technologies from a Safety Perspective [1]"

Automation had a relatively large effect on the overall index with up to a 13% increase in

PEM's overall index and up to a 44% increase in SOEC's control parameter for a 60% change in the parameter value (2.10a). Process monitoring in 2.10b showed there was a notable increase in the overall index with up to a 5% increase in PEM and a 21% increase in the control index for SMR with a 50% change in parameter.

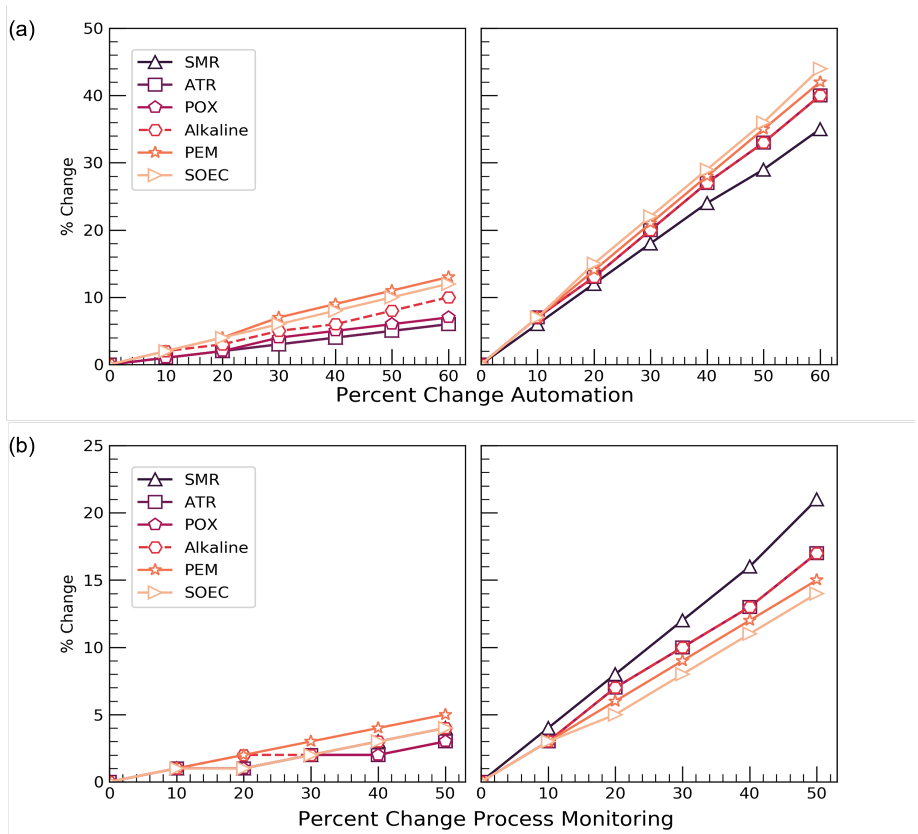

Figure 2.10: Sensitivity analysis results for percentage change of overall index (left) and control index (right) for (a) Automation and (b) Process Monitoring. "Reprinted from Review and Analysis of the Hydrogen Production Technologies from a Safety Perspective [1]"

2.5 Discussion

2.5.1 Results and Sensitivity Analysis Discussion

In this study, we demonstrated the versatility of MCDM by developing a framework which incorporates safety, economic, and environmental benefits and costs. We assigned the importance to three important criteria. This importance is calculated using 3 major indices considering 20 weighted factors. The importance calculated for three criteria are 18.7%, 57.9%, and 23.4%, for the operation, design, and control parameters.

Considering the input data from different sources and the importance of different criteria as mentioned above, SMR is identified as the most preferred technology followed closely by ATR. Widely available feedstock materials and a mature technology are two traits that were well-aligned with prioritizing a highly attractive hydrogen production technology. Point values, however, do not account for the uncertainty in the data and the qualitative scaling values. This is an inherent deficiency in AHP and in MCDM. Different techniques such as sensitivity analysis on weighting schemes [109] and cost-benefit analysis [16] address uncertainties and make more comprehensive analysis. The fuzzy set theory provides a comprehensive framework and better-defined parameters for a robust decision-making model. Fuzzy set theory considers uncertainty analysis and provides a range of results which confirms that SMR and ATR had a smaller uncertainty because of their robust infrastructures and large resources; thus, resulting in a high score of design index. Meanwhile, technologies that scored lower in control or in availability of resource parameters contained larger uncertainty. For example, water-based technologies had a minimal index range of 0.153, which is two times the minimal range of natural gas technology of 0.07. These uncertainties are inherent in the linguistic variables. Nonetheless, these uncertainties reflect extreme cases found in literature and did not significantly affect ranks, which remained the same. As a result, addressing such uncertainties are important. As consensus in these variables becomes more apparent, uncertainty ranges become more precise. Technological improvements and more available data produce the same effect in creating cohesive values.

There was a possibility of rank reversal. Sensitivity analysis quantified the extent of the effect that availability of resource, process monitoring, and automation had on results. For example, a significant drop in the value of the availability of resource parameter reduced the overall index of up to 42%. A disruption in the supply chain would change the attractiveness of a given technology. To maintain the rankings, it is imperative to prevent such major disruptions from occurring. Meanwhile, current density, degradation, production rate, and energy efficiency parameters contained in the operation index exhibited insensitivity. In summation, individual parameters in the operation index had negligible effects while the design and control indices proved to be the major contributors toward the overall index.

2.5.2 Comparison with Other Results and Clarifications

To place the current work into the general context of the literature, the parameters that had a noticeable effect on the technologies' desirability were compared. These include: availability of resource, longevity of system, safety of operation, process monitoring, and automation.

1. *Availability of resource* - The absence of a standardized scale in determining the resources used in one technology was a challenge when choosing the appropriate scale of such technology. This resulted in a qualitative determination of available resources. For example, natural gas feedstock and nickel catalyst used in SMR are more widely available and 100 to 150 times less expensive than noble metal counterparts [110]. Simoes and co-workers found that water availability if assumed to be from natural sources were insufficient for electrolytic production [111]. Therefore, long-term electrolytic production on par with SMR production would not be possible. However, alternative sources of water treatment such as wastewater and lower-quality water sources could change the production landscape. This analysis is not limited to feedstock. Highly specialized, uncommon materials such as yttrium and zirconium as electrode materials contribute to a lower rating. Additionally, technologies requiring extra materials such as pure oxygen, in the case of POX, or highly specialized materials, result in a lower rating. SMR and ATR's ratings were comparatively higher than those for the other technologies because they had higher amounts of available feedstock and catalyst supports.

2. *Longevity of system* – Since plants are typically expected to last for 25 years to be economically feasible, all plants were assumed to have an average of 25-year lifespan.

3. *Safety of operation* – The safety of operation was qualitatively determined based on the types of possible accidents and the exposure to dangerous conditions during the hydrogen production process. SMR being more susceptible to explosions and more intense and complicated

than the others, was deemed higher consequence. Additionally, high temperature and pressure operations require better process control and more robust materials to minimize safety liabilities [112]. High pressure electrolytic operations add risk to hydrogen-oxygen mixtures, which must be closely monitored [32].

4. *Process monitoring* – Understanding the overall operation parameters and optimizing such conditions for a given technology require significant time and research. More predictable and controllable parameters in technologies such as SMR and alkaline electrolysis results in a high score. Technologies that are not well understood, usually newer and not commercially available, like SOEC receive a lower rating. The rating given corroborates with the literature that states that SMR have been thoroughly studied to monitor real-time process and evaluate potential processes [113]. Likewise, AE's surface reactions using Ni electrodes are well understood and there are continued efforts toward simulation modeling [114, 115, 116]. Prior efforts have corroborated the assumption the difficulties and additional work necessary in tuning surface temperature in autothermal conditions [117].

5. *Automation* – The amount of possible automation in a technology was determined by the simplicity of the process. For example, a plant which requires less equipment was given a higher score. A technology not yet commercially available like SOEC was given a lower score because the mechanism is not fully understood but is based on well-established pre-existing commercial examples. POX and ATR were given the same score because the reaction can be highly exothermic, making the process potentially more difficult for control configurations to automate. Additional studies state that there AE is well-established and mature, but does require additional control systems for highly autonomy [118]. Saba and co-workers' claim that automation is necessary for market competitiveness, a category that was considered important in this study [119].

We note that other studies involving MCDM with similar parameters as listed above have been reported in the literature. However, the findings from the current study are different from those that have previously been reported. For instance, Acar and co-authors have used MCDM to compared renewable and nonrenewable hydrogen energy options [18]. They found that the highest weighted parameters were efficiency, control, and raw material parameters. While their results also considered nonrenewable hydrogen energy to be the most ideal, they omitted the safety and environmental factors, which from our work, have been found to play an important role in the decision-making process. A recent work by Abdel-Basset and co-authors in which technical, resource, economic, social, and environmental parameters were weighted, environmental impact was found to be most important parameter [120]. This is in part in agreement with our findings except they omitted the safety aspect, which was found to be highly important in our work. These findings show that changing the weighting scheme can affect the end results.

2.6 Conclusion

We used AHP to provide a mechanism for choosing the most appropriate hydrogen production technology by quantitatively comparing the different type of hydrogen production technologies. The comparative evaluation integrated with criteria was proposed through the LInX decision-making system to identify the most appropriate technology when accounting for safety, feasibility, and controllability throughout the technology's life cycle. The collected data were analyzed for technology status and performance in categories encompassing design, operation, and control. Quantifiable parameters utilized scales based on economies of scale and qualitative parameters containing a subjective scaled rating. The weighting scheme in AHP was prioritized considering the technology, feasibility, and safety. For example, the technological maturity, safety, and controllability were more heavily weighted than parameters in the operating conditions. Integrating safety and controllability in a risk-based analysis provides a more thorough decision-making model. This results in creating a clear and comprehensive method that is dynamic as technology continues to improve. The results showed that the design index had the most significant impact, accounting for about 50% of the technology's index. This supports the fact that the emphasis was based on the feasibility of the technology. Parameter values are relatively similar due to improving technology making process and operating conditions more competitive. However, the necessary infrastructure and resources largely contributed to this decision-making process. The findings showed that SMR technology is not the highest rated in terms of safety or automation. However, SMR's well-understood process makes monitoring more predictable and better understood than competing technologies. By using uncertainty analysis, we observed that the index values were relatively robust with SMR and ATR while other technologies had a larger range of index uncertainty. The major deciding factor in this calculation was the lower uncertainty in feedstock or catalytic material supply. The sensitivity analysis showed that the availability of resource parameter could cause up to a 41% decrease in the technology's index while other sub-indices had a less significant impact, primarily in the operating conditions category. For example, production rate and levelized cost both had non-negligible contributions to the operating conditions index, but still had negligible impacts on the overall index. The control index that contained process monitoring and automation had a high impact on the category index and a moderate impact on the technology's overall index. Overall, these findings can be applied to more systems and the model can be improved to include probabilistic distribution variables dependency to attain results with less uncertainties. Future works in this area should involve improvement in the uncertainty analysis and consequences. Also, more parameters and technologies can be introduced and allow future opportunities for a more comprehensive review.

3. Process Risk Index (PRI) – a methodology to analyze the design and operational hazards in the processing facility [1]

3.1 Introduction

The consequences of catastrophic incidents are severe, and chemical industries can lose upwards of hundreds of millions or billions of dollars per incident [121]. The probability and impact of catastrophic incidents can notably decrease with proper safeguards and considerations. Conducting such prevention plans begin throughout and after the design process, which offers multiple methods. This includes quantitative risk analysis such as probabilistic models. Using such methods requires an extensive amount of data and information. Another method is a heuristic-based approach, which acknowledges that not all data is present, thus, humans must use some subjectivity in their decision-making. This approach is common in industries such as investing, but its principles and relevance extend to process safety risk assessments [122, 123]. Hazard and Operability Study (HAZOP) is among the most popular heuristic methods of studying safety throughout a plant life cycle [124]. A traditional HAZOP procedure contains plant layouts; analyzes chemical data; uses guidewords to characterize deviations; and identifies all relevant nodes. Despite its popularity, HAZOP requires a significant amount of time and effort and process information [125].

Additionally, HAZOP is not a quantitative technique that computes relative or absolute calculations. An alternative and less rigorous approach involves having risk matrices. Its main advantage is allowing a quicker decision-making process and emphasizing prioritization. The matrix has a region that characterizes negligible, low, medium, high, and extreme risks. Risk matrices' disadvantage, however, is that their uncertainty is not always known, and biases could affect the accurate risk determination [126].

[1] Currently under review by the journal *Process Safety and Environmental Protection*

3.1.1 Safety Indices

Using a safety index is a proposed risk assessment approach because it is quantitative, time-efficient, and flexible for decision-making. Khan and Abbasi highlight the most substantial advantages of using safety indices as [2]:

- An efficient means of hazard identification;
- Provides net scores that are comparable in risk levels and hazards posed;
- Net scores are comparable with alternatives; and
- They do not require the user to have a high level of expertise.

Roy et al. states that different safety indices screen for specific hazards ranging from explosion to risk throughout a plant's life cycle [124]. The Dow Fire and Explosion Index (F&EI) is well-established and widely used in risk assessment for fires and explosions [127]. Its limitations are its significant reliance on material factors and its neglect of other risk factors, such as unit operating conditions [128]. Khan and Abbasi developed the fire and explosion damage index (FEDI) to improve upon the F&EI and considers the danger of operation on a unit-by-unit basis [2]. The FEDI's major improvements include adding physical energy factors such as temperature and pressure into hazard calculations. This addition is implemented into the hazard identification and ranking (HIRA) system for hazard analysis. The safety-weighted hazard index (SWeHI) improves upon the HIRA system and considers human factors and safety control systems. Although more comprehensive, this study requires extensive information not readily available [129]. Other safety indexing studies, such as the integrated safety index (I2SI), assess the process design's hazard potential and economic evaluation [130]. Safety indexing also extends to relative risk calculations. Shariff et al. propose a process stream index (PSI) as an inherent safety assessment tool for streams using thermodynamic and operating data [131]. One aspect of the PSI is normalizing parameters of interest (i.e., temperature, pressure, density, and combustibility) concerning their averages. The relative stream risk rankings are compared, and the highest risk stream is identified.

3.1.2 Motivation and Application of Current Work

While extensive literature covers a range of risk indices, there is a gap in creating a methodology that implements risk mapping using a heuristic-based approach. This work highlights the overall process risk by making the Process Risk Index (PRI) and proposes solutions when operating condition deviations occur. Creating an indexing method is important because it contains measurable metrics not found in risk matrices but does not always need to require extensive information found in HAZOP. Khan et al. discuss and implement a color-scale adopted in risk matrices to create a safety performance index and monitor lagging and leading safety indicators [132]. Thus, integrating a risk map with the PRI provides a diagnostic tool for observing process deviations. Utilizing this helps identify the risk and diverging operating conditions of respective regions [132]. Creating an early warning system design is important in avoiding catastrophic events and provides possible corrective actions to adjust for deviations.

We implement risk indices using hydrogen production as a case study. Hydrogen is a promising energy carrier with a high energy density and does not emit carbon when combusted [1]. Although promising, hydrogen poses major safety concerns. Hydrogen has a high flammability range, can permeate through traditional storage vessels, and contains low minimum ignition energy (0.02 mJ) [133]. Safety studies note its reactivity and combustibility with hydrocarbons such as methane, propane, ethane, and others when mixed with air [134, 135]. This study uses steam methane reforming (SMR) because it is a well-established and the most popular hydrogen production method. The risk profiles are adjusted specific to the SMR plant and recorded at varying operating conditions to reflect both the individual unit and the overall system risk.

The remainder of this study is structured in the following manner: Section 2 describes the methodology, the elements behind the PRI risk profile, and risk mapping. These profiles are implemented in an SMR plant as a case study. Section 3 presents the risk mapping results for the SMR process and benchmarks with the FEDI. Section 4 concludes the work.

3.2 Methodology

This study implements a knowledge-driven, logic-based framework to analyze the safety of a hydrogen production process. The framework provides distinct advantages because it is easy to implement and understand, operational in nature, and allows a root cause diagnosis of safety hazards. Subjective analysis, a standard limitation in this framework, is addressed by adopting a systematic methodology and is presented in Figure 3.1 [122]. The methodology comprises three core steps: Process Risk Identification, Process Risk Analysis, and Process Risk Management. The overall process risk is composed of risk indexes for each unit and considers the worst-case scenario. After risk indexing, the process deviation's synergistic effects on operational units are analyzed using the process simulation tool, Aspen HYSYS. These operational data values are converted into risk values, and their details are described in the subsequent sections. The last step of the methodology is to configure preventive and control actions that minimize the assessed risk from previous steps. This step helps undertake diagnostic analysis and identify the root causes of the risk, which would aid in deciding corrective actions. The details of each step from the methodology are presented in the subsequent sections.

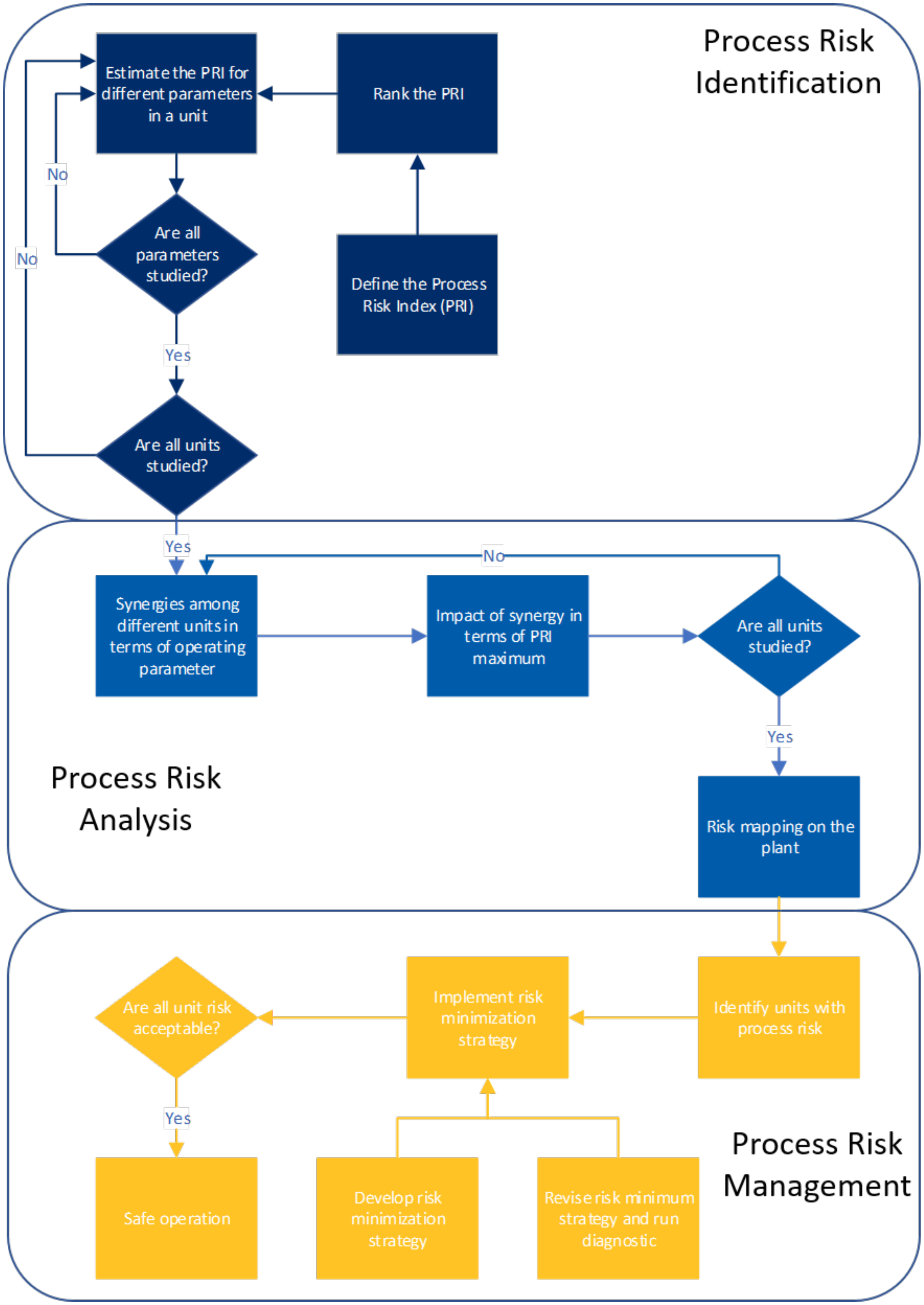

Figure 3.1: Proposed risk identification, analysis, and management framework.

Step 1: Process Risk Identification

Step 1.1. Definition of the Process Risk Index (PRI)

There are different interpretations of risk for a given process. This study defines and bases the PRI on the safety of both equipment and containment of the syngas. Equipment safety can depend on different factors, but the PRI created here defines the risk as damage to the equipment resulting from extreme operating conditions. Therefore, the PRI assesses and prevents equipment deterioration by defining the conditions that border or cross beyond a certain index threshold. Failure to act upon preventative steps causes further complications. For example, a loss of containment can occur and cause a mixture and create explosion hazard risks. The PRI considers a loss of containment, fire, or explosion event as the most dangerous. The subjectivity in the analysis in defining danger for the PRI remains flexible and versatile towards other hazard scenarios.

Step 1.2 Ranking of the PRI

Defining the PRI in this study requires a corresponding ranking system. The ranking scale is defined using a range of values. This study considers the ranking hierarchy to describe the following:

- values between 0 and 2 are within the acceptable risk domain,
- values between 2 and 3 require caution, and unaddressed attention leads to possible equipment damage,
- values above 3 are regarded as dangerous because of definite equipment damage and a potential explosion or fire hazard scenario.

Figure 3.2 captures the risk regions in the PRI, and there are corresponding colors according to each risk region adopted from a traffic light system. These rankings and this color scheme serves as a leading indicator and allows proactivity for process safety design. It needs to be noted that the ranking regimes remain absolute, but the ranking index and risk profile are unique to each process unit.

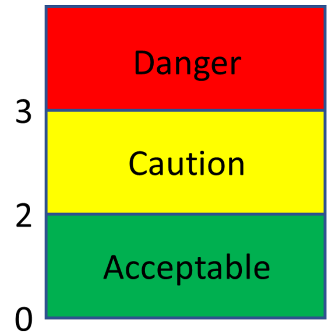

Figure 3.2: Risk level indicators of a given unit.

Step 1.3 Estimation of PRI of a unit

Creating an individualized PRI for each unit allows a comprehensive study of the process. First, a minimum risk value corresponding to an operating parameter is calculated using Equation 3.1. Determining a point value for a parameter is conducted by expert opinion or from literature. If literature proposes a range of optimal operating values, an average of the operating values is considered the minimum risk value. Determining the K constant requires two different considerations: how high parameters operate for a given unit and the type of unit operation. This study considers reaction conditions and high operating conditions as inherently more hazardous. Therefore, conditions that are considered relatively high are riskier.

$$\text{Minimum Risk} = \frac{1}{K} \text{ at an optimal operating condition}$$
$$\text{where } K = \begin{cases} 1 & \text{for initially high parameter regions or reactor vessels} \\ 1.25 & \text{for low regions} \end{cases} \tag{3.1}$$

Deviations in the process occur and require expert opinion and literature to aid in defining the risk value at a node. This study utilizes a linear risk profile for estimating the PRI of a given unit. The advantages of linearity include flexible scaling, ease of implementation, and lower computational intensity. Additionally, the risk profile provides a graphical representation that captures risk values corresponding to each operating parameter value. Using Equation 3.2, the risk profile converts any given operating condition into a risk value. After providing a PRI for each unit, process deviations and synergistic effects are investigated.

$$Risk = \frac{\Delta Risk}{\Delta Parameter} * Parameter + Intercept \tag{3.2}$$

Step 2: Process Risk Analysis

Step 2.1 Synergies among Different Units

Applying and calculating the risk profiles is important to determine the effects and relationships among different units. Evaluating the synergies requires attention because upstream changes affect downstream units. Using the process simulation tool Aspen HYSYS, we change a given operating parameter and record the effects on downstream units. Ranges at which the input parameter is changed must have three considerations:

1. the mole fraction remains constant,

2. the unit parameters downstream are unaffected,

3. the parameter change is infeasible for a respective unit.

The temperature change in the Results section for the SMR example highlights and provides a detailed explanation for choosing extreme parameter values.

Step 2.2 Impact of the Synergies on Process Risk

Once operating condition changes are evaluated, these parameter values are converted into risk values. This study considers the worst-case scenario and uses the Max operator to define the overall facility risk in Equation 3.3. This operator's advantage is its ability to evaluate the risk levels of both individual units and the overall process. For individual units, the Max operator compares the risk values of each unit with respect to the operating parameter (i.e., temperature, pressure, flow). Meanwhile on a process system level, the Max operator adopts the unit with the highest risk as the overall system risk level. Determining the overall risk across all units and the system allows a consensus on the system's safety and allows users to create a risk map.

$$\text{Overall Facility Risk} = \text{Max}(\text{Unit Risk}_i) \quad \text{for i = temperature, pressure, flow} \tag{3.3}$$

Step 2.3 Risk Mapping

Although numerical data is important in comparing the safety of the given nodes in a process, the ranges of acceptable and unacceptable risks are important in determining the process system's safety architecture. Khan et al. create an analogy characterizing driver safety according to certain activities and combinations [132]. In this example, the driver does not know the extent of parameters contributing to driving safety calculations. Instead, they know only whether their behavior is within the recommended regime. Likewise, process safety is multifaceted; simplifying initial assessments and providing a front-end screen tool is the initial objective. We increase the diagnostic efficiency, using traffic-light colors in Figure 3.2, and provide a visual risk indicator. Once appropriate mapping is possible, establishing safe conditions despite riskier operating conditions is integral in attaining process risk management.

Figure 3.3 provides a simple example of a water and benzene separation system containing operating conditions. There is a pump (P-100), heater (E-100), and separation system (V-100). According to the risk map, the overall system risk is considered safe and at a minimum risk. The constraint in this system is that temperatures deviating above 200°C for any unit would be high risk.

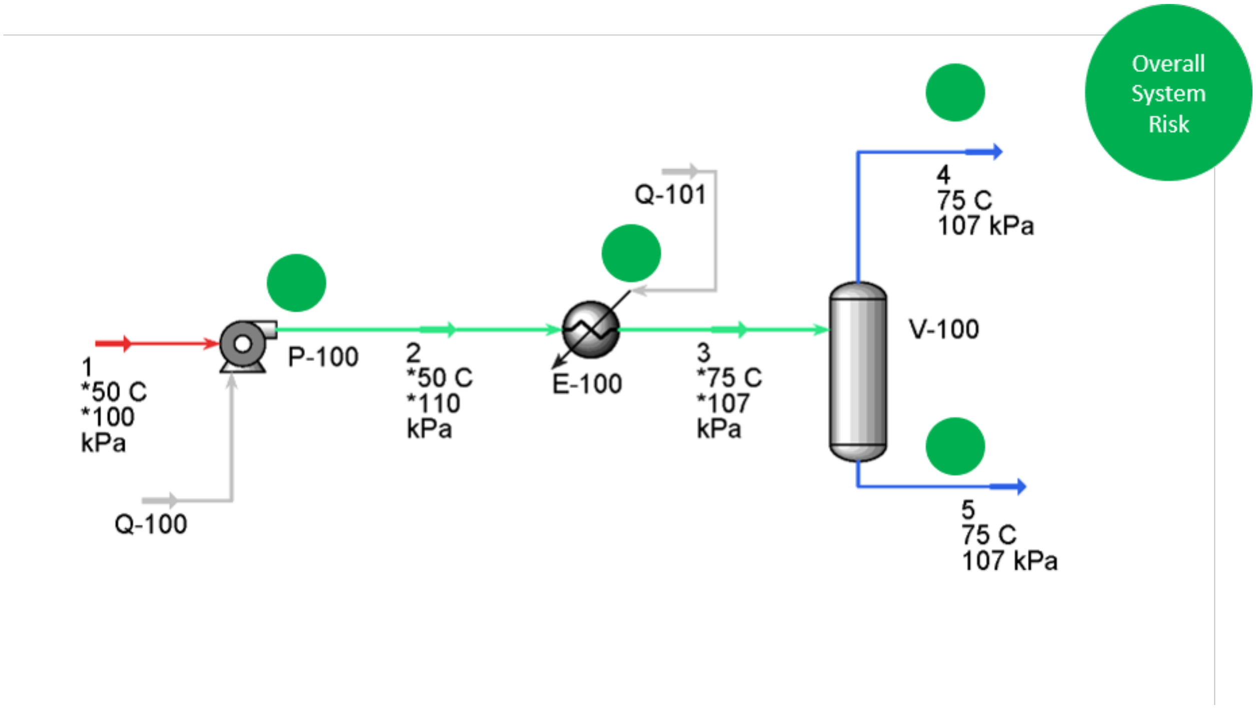

Figure 3.3: Risk mapping example of a pump, heater, and separator system of benzene and water.

Step 3. Process Risk Management

Step 3.1 Identify Units with Critical Process Risk

System deviations and disturbances often change once low-risk operations into risky ones. Identifying which units are affected by aberrations allow safety implementation strategies. Using the same example, the flow deviates and increases from 500 to 1500 kg/hr. Figure 3.4 shows the system is now considered unsafe. Performing root cause analysis on the problem is streamlined using the provided risk map. E-100 and V-100 are identified as the two most risky operations in this process. Initial screening shows that temperature and pressure are unaffected, but the risk index determines an overflow of fluid is operationally hazardous and damages equipment. Further investigation reveals the disturbance begins at P-100 with a high flow rate and allows decision-makers to develop a risk minimization strategy.

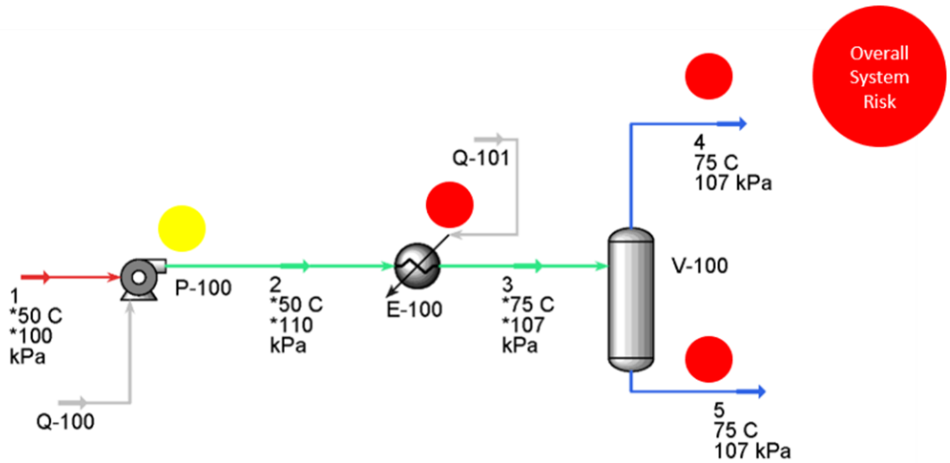

Figure 3.4: An example of unsafe conditions.

Step 3.2 Develop Risk Minimization Strategy

The ideal objective is to create a system that accounts for most deviations and corrects the compromised system into an acceptable safety regime. Therefore, the constraint in this example is to decrease the risk despite having a high flow rate. The pump's risk will remain cautious because its flow cannot be changed. However, downstream units' risks (E-100 and V-100) are reducible by adjusting flow to an acceptable threshold. Therefore, risk experts may propose a few flow regulation strategies and create diverging streams, bypass streams, recycle streams, or valves. These proposed solutions could be individually implemented, and its effects are explored in the risk minimization strategy. It should be noted that creating new process units will require additional risk indices and indicators.

Step 3.3 Implement Risk Minimization Strategy

This strategy implements corrective actions and suggests, in this example, to create a separate stream. Figure 3.5 shows the system risk is downgraded to caution. Additionally, the heating and separation risk unit is downgraded to an acceptable risk level. Although not ideal, the warning indicator allows operators time to diagnose and fix the root cause before catastrophe occurs. We can implement and compare other proposed strategies before deciding on the most practical and effective solution. Therefore, using the PRI as a diagnostic tool to understand the solution's effectiveness allows for an adequate process safety method.

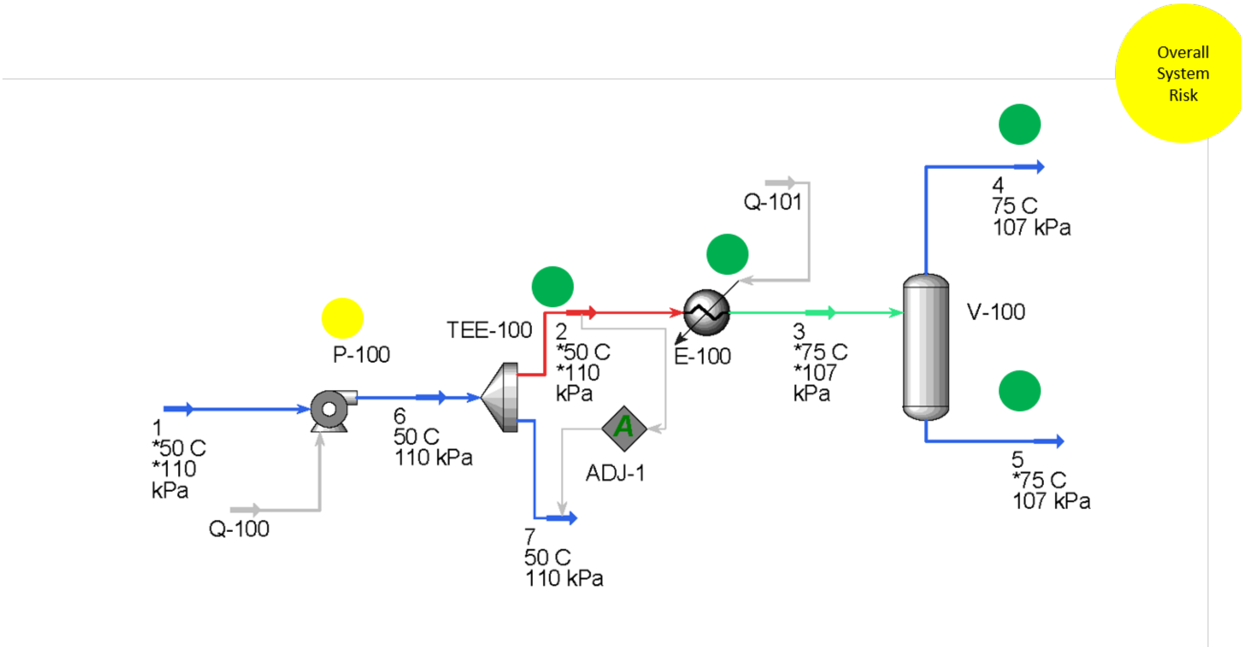

Figure 3.5: Corrective actions, for example, flow problems. Note that the risk is not green due to the high pump flow. The risk is minimized for more extreme cases.

3.2.1 Application of the Methodology

A simple case study implements the SMR process into the above methodology. The SMR process is designed using Aspen HYSYS and according operating conditions based on literature [136, 137, 70, 69, 138]. The description of the process is elaborated upon in the following text.

Steam and methane are the two primary compounds in the SMR process. The incoming streams are mixed at different temperatures and undergo a reforming reaction (Equation 3.4). This reaction produces hydrogen and carbon monoxide. The water-gas shift (WGS) reaction minimizes carbon monoxide byproducts and reacts carbon monoxide with steam to produce additional hydrogen (Equation 3.5). A high and low-temperature WGS reaction requires different catalysts and membranes which result in different temperature capabilities [139]. Coolers are implemented throughout this process to prevent overheating. The unreacted steam is condensed and separated from the syngas. The final purification step of hydrogen occurs using a Pressure Swing Adsorption

(PSA) unit, which splits the hydrogen from its impurities (CO, CO_2, and CH_4).

$$CH_4 + H_2O \rightleftharpoons 3H_2 + CO \tag{3.4}$$

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \tag{3.5}$$

A separate risk unit profile is created to reflect the risk of a given unit. Figure 3.6 is an example of the reforming unit's risk profile. After recording all units' risk profiles, the operating conditions are tested across different operational parameters. The updated risk values adjust with the operating parameters from the synergistic effects. The *Results* section reflects the modified operating conditions at a given unit or stream and its effect on relevant units.

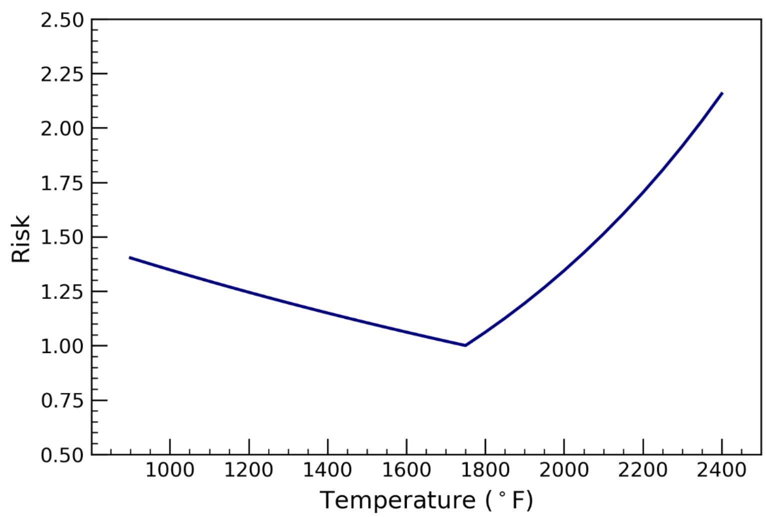

Figure 3.6: The risk profile for reforming unit. Note that the risk value is 1 because of its inherently higher operating temperature. The minimum is established at 1750°F, and the asymmetry is due to higher risk at higher temperatures.

3.2.2 Assumptions

Linearity is assumed to allow simplicity in calculations. The unit risk levels are grouped with their respective outlet streams. Lower absolute parameter values contain more symmetric risk profiles than high parameter values or unit reaction operations. Lastly, this case study considers pressure conditions well within safe operating conditions and would not affect the overall risk.

3.3 Results and Discussion

Identifying the hazard scenarios using recommended configurations provides a base case and should be considered within an acceptable safety level. As shown in Figure 3.7, the risk map for the base case situation confirms that all unit operations are within the safety parameters.

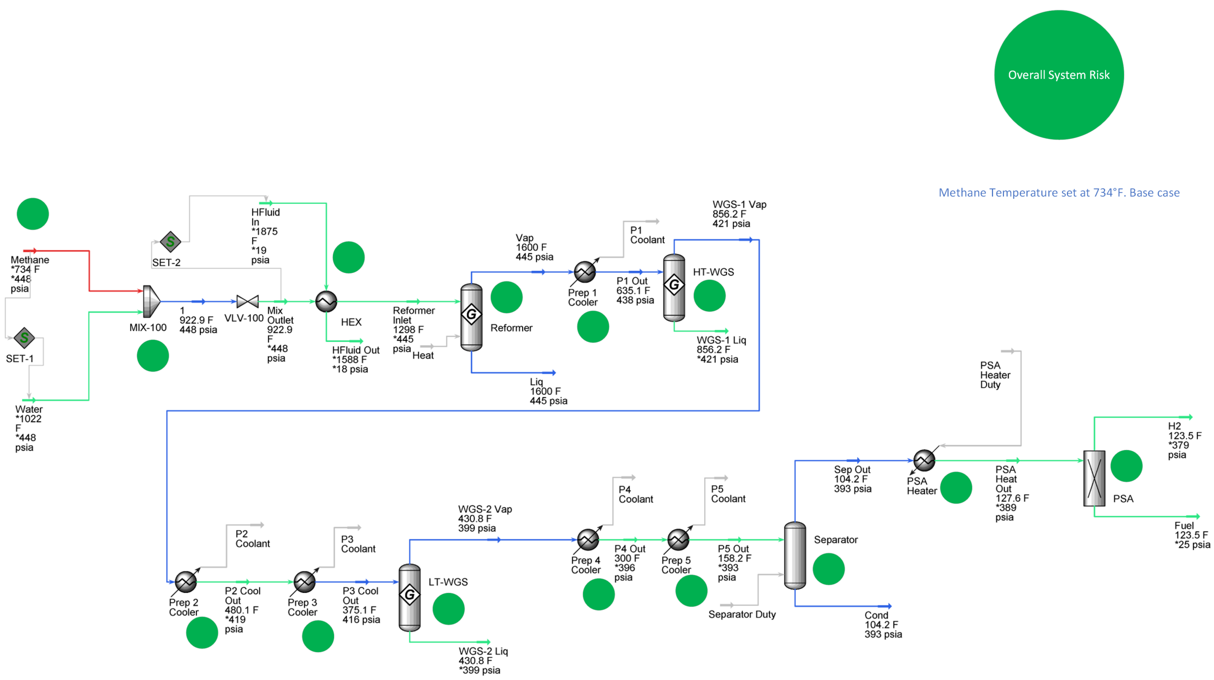

Figure 3.7: The base case of the SMR process. As indicated, the operation is considered within the "Acceptable" boundary.

Defining extreme parameters require discretion through process simulation observations. We consider extreme parameter changes at points where mole fractions remain constant, unit operations downstream remain unaffected, or infeasible operating condition changes. Mole fraction consistency occurs in situations such as uncontrolled heating. Once mole fractions remain consistent, pure heating often occurs and can sometimes lead to exponential temperature profiles, a major safety concern. This study defines temperatures values before such profiles occur as extreme. The second consideration considers when an increase in one parameter does not affect downstream parameters. Increasing the feedstock rate, for example, causes an exponential decay in downstream temperature. The extreme value is defined as the feedstock rate value at which all temperatures downstream remain unaffected. The final discretion is an unrealistic change. If all upstream units work properly, a cooling unit will not operate at higher temperatures than its inlet. Therefore, the maximum temperature and extreme parameter change are constrained to its inlet temperature.

Figure 3.8 displays a scenario such that the reformer outlet reflects uncontrolled heating and considers the operation as a dangerous risk. The reformer unit is not considered hazardous, likely because of its typically wide and inherently high-temperature operation range. If continued heating occurs, the reformer's PRI will become hazardous. The synergies highlight more dangerous downstream effects. The HT-WGS reactor, LT-WGS reactor, and cooler four are considered the most hazardous equipment in the plant. The high-risk rating is reflected and is explained through the WGS reactors' inherent risks. This reason is that the WGS units have a sensitive membrane, limiting the operation to a narrower temperature range and an exothermic reaction whose temperature will continue increasing. As a result, leakages and undesirable explosive mixtures can notably deviating conditions. Cooler 4 is considered dangerous in this scenario because its temperature is significantly higher than normal operation; this increase risks cooler failure and leads to a possible loss of syngas containment. Its subsequent cooler allows the operation to be relatively safer and is identified as requiring caution. At the most downstream section, the PSA preheater and the PSA unit are considered safe. This categorization is due to the assumption that the units are safe so long as the operating temperatures are below hydrogen's autoignition temperature (1085°F) [140]. This scenario displays that the physical unit operations of coolers and heaters requires serious consideration but are considered at a lower risk than unit operations. To address high-temperature corrective actions for the reactor units, redundancies are necessary for this system. One proposed action is adding a cooler after the reforming process to reduce the cooling load. Another possibility is to reduce the feedstock amount, but this is not appropriate because it reduces the production rate and the economic viability of production. From this case scenario, addressing the root cause, reformer outlet temperature control, reduces the possibility of compromised operational safety.

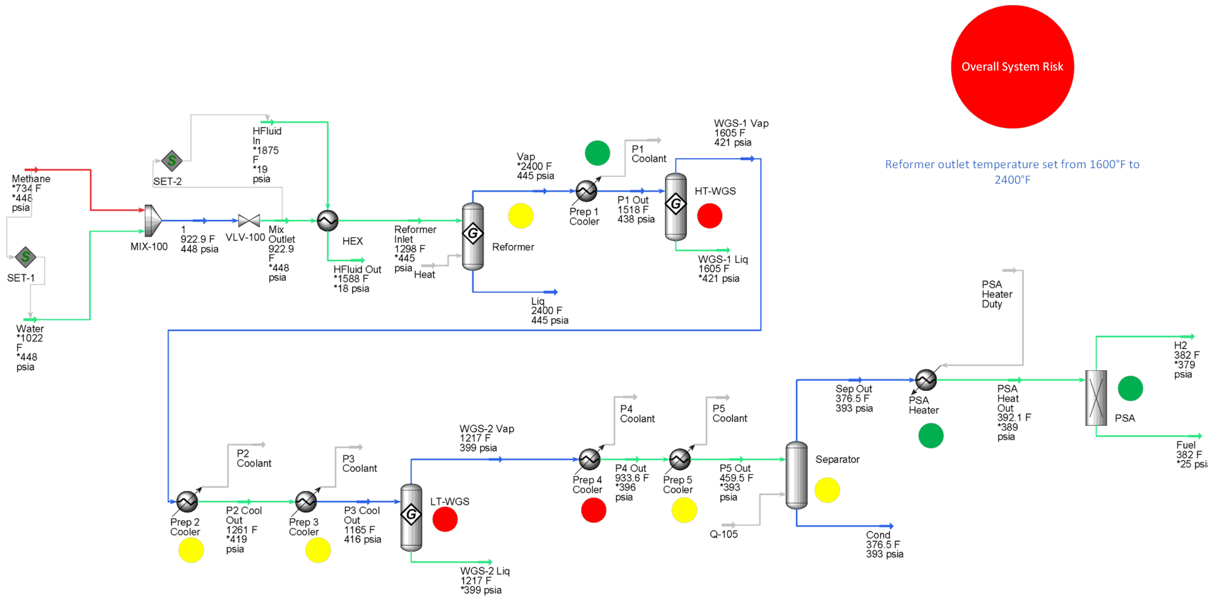

Figure 3.8: An increase in reformer operation from 1600 to 2400°F. This scenario is possible through runaway vessel heating.

Likewise, low temperatures highlighted in Figure 3.9 affect operational safety. Cooling to 500°F is considered hazardous because it would affect subsequent downstream operations like the HT-WGS. Koc et al. determine that HT-WGS temperature units operating lower than 572°F on the inlet are hazardous because of membrane embrittlement and affect reactor performance [141]. A risk minimization proposal is to avoid the possibility of extremely low-temperature conditions by reducing the cooler power capacity. This suggestion would result in both energy savings and safer operations.

It should be noted that inadequate cooling would cause complications like the previous high-temperature reformer scenario. Nonetheless, using the PRI as a screening method allows future consideration of more detailed plant design methods that comprehensively consider process deviations. The risk map shown in this study enables a quick diagnostic tool that captures hazard

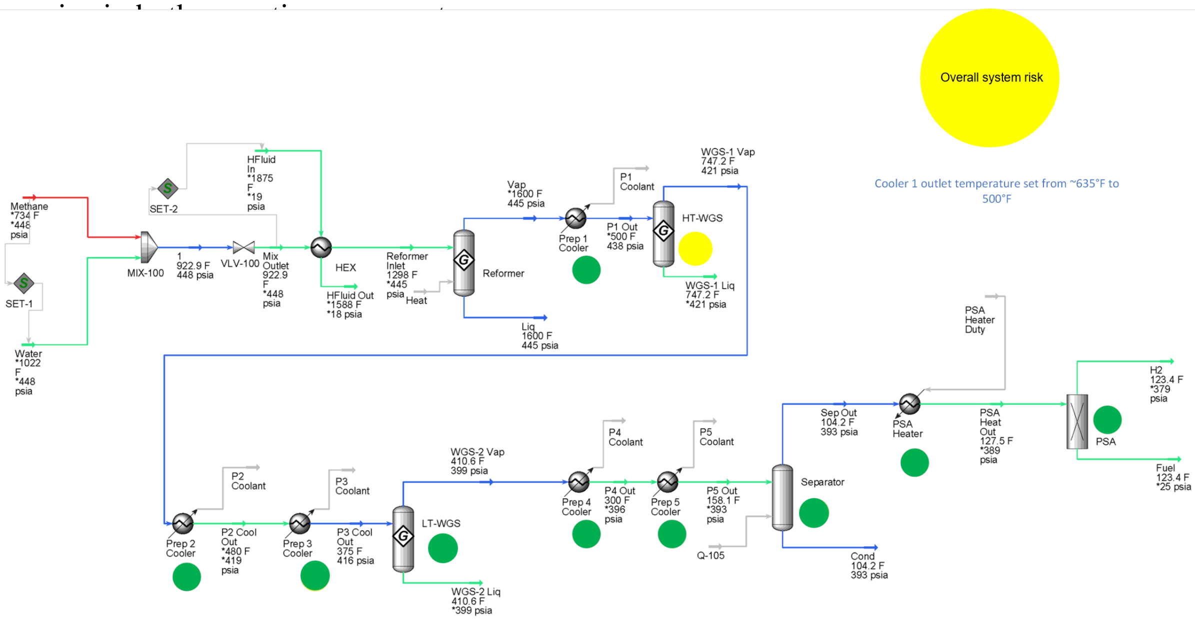

Figure 3.9: Cooler 1's case study shows the PRI considers that too low temperatures cause safety concerns in HT-WGS operations.

Table 3.1 summarizes the safety index results based on process simulation. One notable effect is that both coolers must fail to categorize within the "Danger" or "Caution" level. This is highlighted with a standalone failure of cooler 2, which does not affect the overall system risk. However, having an extra cooling unit would reduce the contingent risk when both coolers fail. From this table, the most common hazardous units are the reformer, separator, and WGS units, and extreme process changes often lead to a dangerous scenario. Additionally, moderate changes in the flow require caution, but continued negligence creates hazardous risks. Using the PRI and risk mapping, we can identify the root causes for hazards and begin planning appropriate changes for deviations.

Table 3.1: Summary of Results

Parameter Change	*Units at Risk*	*Overall System Risk*
Base Case	**Acceptable:** All units	Acceptable
Reformer Temperature (1600 to 2400°F)	**Caution:** Reformer, Cooler 3, Cooler 5 **Danger:** HT-WGS, Cooler 2, LT-WGS, Cooler 4, Separator	Danger
Prep 1 Cooler Temperature (635 to 1500°F)	**Caution:** Cooler 3, Cooler 5 **Danger:** HT-WGS, Cooler 2, LT-WGS, Cooler 4, Separator	Danger
Prep 1 Cooler Temperature (1022 to 500°F)	**Caution:** HT-WGS	Caution
Methane Flow (1000 to 2500 lb/hr)	**Caution:** HT-WGS, Cooler 2, LT-WGS, Cooler 4, Cooler 5, PSA Heater **Danger:** Separator	Danger
Methane Temperature (734 to 2400°F)	**Caution:** Mixer, HT-WGS, Cooler 2, LT-WGS, Cooler 4, Cooler 5, PSA Heater **Danger:** HEX, Separator	Danger
Water Temperature (1022 to 1500°F)	**Caution:** HEX Outlet	Caution
Prep 2 Cooler Temperature (480 to 650°F)	**Acceptable:** All units	Acceptable
Prep 3 Cooler Temperature (375 to 856°F)	**Caution:** LT-WGS, Cooler 4, Separator	Caution
Prep 4 Cooler Temperature (300 to 405°F)	**Caution:** Separator	Caution
Prep 5 Cooler Temperature (158 to 430°F)	**Caution:** Cooler 5, PSA Heater, PSA **Danger:** Separator	Danger
Separator Temperature (104 to 430°F)	**Caution:** Separator, PSA Heater	Caution

Benchmarking Study

We benchmark the PRI with the FEDI. As introduced, the FEDI is more comprehensive than the widely used F&EI because it includes calculating the thermodynamics and operating unit conditions. The FEDI's calculations are specified in Khan and Abbasi's hazard identification and ranking model [2]. This SMR process contains three unit groups: reactors, physical operations, and other hazardous units. Different types of units have unique approaches to calculating the significant factors and the penalty scores. There were several assumptions made in this study. (i) The chemical with the most dangerous NFPA score was adopted in pn4. (ii) The unit density is considered as 70% for pn7. (iii) Distance from the next hazardous unit is 80 meters. (iv) The entire syngas production process is a gaseous phase. After considering all penalties and contributing physical and chemical factors, the damage potential is calculated and converted into the FEDI using Equation 3.6 [2]. The FEDI values for each unit are evaluated using Table 3.2.

$$FEDI = 4.76(\text{damage potential})^{\frac{1}{3}} \tag{3.6}$$

Table 3.2: Hazard Ranking for the FEDI[2]

Fire and explosion damage index (FEDI) value	Hazard characterization
FEDI>500	Extremely hazardous
400 <FEDI <500	Highly Hazardous
200 <FEDI <400	Hazardous
100 <FEDI <200	Moderately hazardous
20 <FEDI <100	Less hazardous
Else	No hazard

Table 3.3 displays the PRI and the FEDI benchmarking results using the same process condition changes as Table 3.1. The FEDI results show that 8 out of 13 units are considered hazardous in the base case scenario. This contrasts with the PRI, which considers all units as safe. Another finding is the FEDI's insensitivity towards operational changes, and its results have minimal changes in hazard characterization, updating 10 out of 13 as hazardous. The high heat of combustion explains this risk rating result as notably influenced by the syngas mixtures. The FEDI considers the mixtures inherently hazardous and a large potential damage impact upon the mixture release. This danger level is magnified from hazardous to highly hazardous when the feedstock increases. This

change upgrades the FEDI classification to 12 out of the 13 units as highly hazardous because of the index's high sensitivity to flammable gas quantity. Although still considered dangerous, the PRI, in comparison, lists 1 out of the 13 units as dangerous upon feedstock increase. The reason for the discrepancy in the analysis is that the PRI development considers other factors as equally important. Assuming the quantity does not enter a hazardous operating condition, most units with increased methane flow require attention, but serious focus is directed towards the separator unit. Another notable result from this benchmark study is the lack of influence operational temperature increases have on the FEDI hazard ranking. Ortiz-Espinoza et al. investigated the FEDI and reached a similar conclusion by stating that the FEDI is heavily dependent on mass factor in unit hazard classification [128]. Therefore, the FEDI is not successful in screening for hazards when deviating operating conditions occur. The PRI is an improvement in capturing operational risks and shows which changes affect system safety. Additionally, the PRI is more appropriate in finding that improper operation could cause a cascade effect that magnifies the risk in downstream units. Thus, the PRI is an improvement from the FEDI in diagnosing operating condition deviations, finding the root cause of deviations due to its increased sensitivity, and determining the overall system risk.

Table 3.3: Comparisons between the PRI and the FEDI. The highest risk units and respective values are grouped. The respective percent change is recorded on the adjacent column on the right.

Parameter Change	*Units at Risk*	*Overall System Risk*	*Units at Risk*	*Overall System Risk*
	Process Risk Index		*Fire & Explosion Damage Index*	
Base Case	**Acceptable:** All units	Acceptable	**Hazardous:** Reformer, Cooler 1, HT-WGS, Cooler 2, LT-WGS, Separator, PSA Heater, PSA	Hazardous
Reformer Temperature	**Caution:** Reformer, Cooler 3, Cooler 5 **Danger:** HT-WGS, Cooler 2, LT-WGS, Cooler 4, Separator	Danger	**Hazardous:** Reformer, Cooler 1, HT-WGS, Cooler 2, Cooler 3, LT-WGS, Cooler 4, Cooler 5, Separator, PSA Heater, PSA	Hazardous

Table 3.3 (continued)

Parameter Change	*Units at Risk*	*Overall System Risk*	*Units at Risk*	*Overall System Risk*
	Process Risk Index		*Fire & Explosion Damage Index*	
Prep 1 Cooler Temperature (High)	**Caution:** Cooler 3, Cooler 5 **Danger:** HT-WGS, Cooler 2, LT-WGS, Cooler 4, Separator	Danger	**Hazardous:** Reformer, Cooler 1, HT-WGS, Cooler 2, Cooler 3, LT-WGS, Cooler 4, Cooler 5, Separator, PSA Heater, PSA	Hazardous
Prep 1 Cooler Temperature (Low)	**Caution:** HT-WGS	Caution	**Hazardous:** Reformer, Cooler 1, HT-WGS, Cooler 2, Cooler 3, LT-WGS, Cooler 4, Cooler 5, Separator, PSA Heater, PSA	Hazardous
Methane Flow	**Danger:** Separator	Caution	**Highly Hazardous:** HEX, Reformer, Cooler 1, HT-WGS, Cooler 2, Cooler 3, LT-WGS, Cooler 4, Cooler 5, Separator, PSA Heater, PSA	Highly Hazardous
Methane Temperature	**Caution:** Mixer, HT-WGS, Cooler 2, LT-WGS, Cooler 4, Cooler 5, PSA Heater **Danger:** HEX, Separator	Danger	**Hazardous: Reformer, Cooler 1, HT-WGS, Cooler 2, LT-WGS, Separator, PSA Heater, PSA**	Hazardous
Water Temperature	**Caution:** HEX Outlet	Caution	**Hazardous:** Reformer, Cooler 1, HT-WGS, Cooler 2, Cooler 3, LT-WGS, Cooler 4, Cooler 5, Separator, PSA Heater, PSA	Hazardous
Prep 2 Cooler Temperature	**Acceptable:** All units	Acceptable	**Hazardous:** Reformer, Cooler 1, HT-WGS, Cooler 2, Cooler 3, LT-WGS, Cooler 4, Cooler 5, Separator, PSA Heater, PSA	Hazardous

Table 3.3 (continued)

Parameter Change	Units at Risk	Overall System Risk	Units at Risk	Overall System Risk
	Process Risk Index		*Fire & Explosion Damage Index*	
Prep 3 Cooler Temperature	**Caution:** LT-WGS, Cooler 4, Separator	Caution	**Hazardous:** Reformer, Cooler 1, HT-WGS, Cooler 2, Cooler 3, LT-WGS, Cooler 4, Cooler 5, Separator, PSA Heater, PSA	Hazardous
Prep 4 Cooler Temperature	**Caution:** Separator	Caution	**Hazardous:** Reformer, Cooler 1, HT-WGS, Cooler 2, Cooler 3, LT-WGS, Cooler 4, Cooler 5, Separator, PSA Heater, PSA	Hazardous
Prep 5 Cooler Temperature	**Caution:** Cooler 5, PSA Heater, PSA **Danger:** Separator	Danger	**Hazardous:** Reformer, Cooler 1, HT-WGS, Cooler 2, Cooler 3, LT-WGS, Cooler 4, Cooler 5, Separator, PSA Heater, PSA	Hazardous
Separator Temperature	**Caution:** Separator, PSA Heater	Caution	**Hazardous:** Reformer, Cooler 1, HT-WGS, Cooler 2, Cooler 3, LT-WGS, Cooler 4, Cooler 5, Separator, PSA Heater, PSA	Hazardous

3.4 Conclusions

This study proposed a process risk index (PRI) and used it to map risk scenarios in an SMR hydrogen production process. The PRI was a heuristic-based approach that estimated the risk for all units considering chemicals involved, quantity, and other related characteristics. The PRI is classified into three tiers: acceptable, caution, and danger. These tiers corresponded to traffic light colors which were implemented into a risk map and updated according to process deviations. We considered the worst-case scenario and used the Max operator to consider the highest risk parameter of each unit. Applying the PRI provided users with a method to identify units with critical process risks. Furthermore, such information allowed an appropriate response to address root causes and minimize the process operational risk.

The SMR process was chosen because it was the most popular and a well-established hydrogen production method. The process consisted of two reaction units (reformer and water-gas shift) and coolers, separators, and heaters. This study used process simulation to gather data on synergistic relationships between the different units. The PRI converted the process conditions into risk values and helped identify the unsafe operational envelop in different units and components. As a result, the SMR process was broken down into individual components to help identify the root cause of hazardous conditions. An additional cooling unit helped improve process safety performance, given that one cooler failed. According to the PRI, uncontrolled reformer temperatures was considered the most dangerous, classifying 8 out of 13 units as hazardous or dangerous. The separator unit was the most common source of unsafe conditions. Its susceptibility to higher temperatures and high syngas content led to an increased likelihood of a catastrophic event. Application of the PRI assists in identifying the process deviations that affected the safety performance of SMR units. It provided a clearer representation of what process risks to address to improve operational safety.

This study benchmarked the risk calculations (PRI) against the widely used Fire and Explosion Damage Index (FEDI). Compared to the PRI, the FEDI did not identify the unit-specific risks during operating condition changes. The FEDI considered 8 out of 13 units as hazardous in the base case, whereas the PRI considered all units as safe. The FEDI value increased the number of hazardous units to 11 out of 13 for most parameter changes. Quantity changes affected the FEDI classification the most, and an extreme feedstock change classified 11 out of 13 units as highly hazardous. This scenario highlighted that the FEDI index focused on mass quantities and heat of combustion values and paid less attention to operational characteristics. The PRI had a different approach and considered possible operational hazards and synergistic effects among units. Changes in operating conditions such as temperature, pressure, and others often created a cascade effect which magnified the operational risk. The clearest example was comparing the risk for the water-gas shift unit. Although more prone to a loss of containment at higher temperatures, the FEDI classified the reformer and the WGS units as equally hazardous. However, the PRI determined the WGS unit as more dangerous given its operational sensitivity.

Although this study focuses on SMR, the PRI applies to different production processes and other hydrogen production technologies such as electrolysis. Monitoring operating deviations and planning appropriately will ensure a safer operation. Although the PRI allows for an effective hazard identification process, it has room for improvement. The PRI assumes linearity, but nonlinear risk profiles are possible. Additional work reflecting nonlinear scales would reflect different and more accurate risk results depending on the system. Another improvement is the PRI can dynamically update with plant data. This allows us to see how corrective actions reduce risk in real-time.

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4. Conclusion and Future Work

4.1 Summary

This thesis proposed a method that determined the most suitable hydrogen production method followed by a heuristic-based, risk analysis method that created a risk map for the respective hydrogen technology. The former method utilized a multi-criteria decision making (MCDM) model in finding the best suited hydrogen production technology. Past studies focused on the economics or technological feasibility but diverted their attention away from safety, which this study addressed. After finalizing the decision of the best-suited technology, the process risks were analyzed by creating a safety index known as the process risk index (PRI). The risk values in the PRI were determined using a heuristic-based approach. This approach when coupled with a risk map, allowed decision-makers to identify root cause effects and prepare risk minimization strategies. Integrating this methodology provided a time-efficient but reasonably rigorous safety analysis approach.

In the MCDM modeling study, finding the pertinent information required an extensive literature review that emphasized the design, safety, and feasibility of each hydrogen production technology. Two types of technologies (electrolytic and natural gas) were compared. The results highlighted the best suited hydrogen production technology; uncertainty and sensitivity analyses were performed to determine the results' robustness. The outcome of this study provided decision makers a comprehensive comparison method for choosing a given hydrogen production technology. After deciding upon a technology, using a heuristic-based approach provided a timely analysis of process risks. The PRI considers measurable parameters which include but is not limited to pressure, temperature, and flow. Converting numerical values into a risk map provided an intuitive interpretation of risk and provides a seamless risk analysis process. Case studies for analyzing extreme parameters could be iterated and safety improvements would aim to minimizing the risk in spite of deviations. The PRI was benchmarked with the fire, explosion and damage index (FEDI); the results displayed that the PRI was more sensitive and more suitable in identifying unit-specific hazards from process deviations. Proposing and analyzing the strategy's effectiveness with this method was an important step in ensuring a safe production process. Therefore, integrating a decision-making model then investigating and addressing a technology's key safety challenges created a comprehensive review of determining the best-suited and safest possible technology.

4.2 Conclusions

The main conclusions from this current thesis are respectively categorized as the following.

4.2.1 Review and Analysis of the Hydrogen Production Technologies from a Safety Perspective

This research presented an overview of different types of hydrogen production technologies followed by a decision-making methodology. The goal after a thorough literature review was to determine the best suited technology with respect to the design, operational, and safety parameters. The key finding of this study was that steam methane reforming technology was the highest rated. This result was heavily attributed to the inherent design, maturity, and feedstock availability. The uncertainty of the results and the sensitivity of the parameters were investigated. There was no rank reversal from uncertainty analysis and the natural gas technologies (SMR and ATR) had the smallest uncertainty. Additionally, this study had a reasonably sensitive weighting scheme because of the even distribution in parameter sensitivity. Thus, this study provided a novel and comprehensive approach for integrating safety into decision-making for a production process.

4.2.2 Process Risk Index (PRI) – a methodology to analyze the design and operational hazards in the processing facility

This task model used a heuristic-based approach in risk indexing and combines with risk mapping to create a safer process. The current research implements SMR as the hydrogen production process because it was a well-established hydrogen production technology with an extensive amount of equipment to analyze. Risk indexing was advantageous over traditional safety analysis because it was a flexible and an easy-to-implement method of quantifying risk. Coupling the risk map with the risk indices allowed root cause identification of process deviations and units at risk. Recordable parameters were converted and analyzed in terms of the respective risk values. This study provided decision-makers a methodology, when implementing the PRI and risk map, for implementing safety recommendations from process deviations. The result, when successfully implemented, would allow an adaptable system that accounts for process deviations and continues operating at safe conditions despite extreme process deviations.

4.3 Recommendations

This thesis attempted to develop a practical approach to analyzing the safety of hydrogen production systems. According to the highlighted objectives in this study, the following recommendations are presented for future research tasks (3 for the Chapter 3 study and 2 for the Chapter 4 study):

- Improving uncertainty analysis and safety consequences with better literature data will improve upon the current study.
- Including other technologies and parameters provides a more comprehensive work. For example, implementing social perception and sustainability into the MCDM adds comprehensiveness.
- Having up-to-date information on the hydrogen production technologies' parameters allows the model to reflect the technological advancements.
- Integrating non-linearity allows a more computationally intensive and comprehensive risk scaling method.
- Record the time-dependent effects upon implementing risk minimization strategies using dynamic process simulations.

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