

École polytechnique de Louvain

Unleash the renewable power within ammonia:

Optimization and uncertainty quantification of the
Ammonia-to-Power pathway

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Acronyms

AFC Alkaline Fuel Cell.

AMFC Alkaline Membrane Fuel Cell.

CCGT Combined Cycle Gas Turbine.

FC Fuel Cell.

GHGs GreenHouse Gases.

HT-PEMFC High-Temperature Proton Exchange Membrane Fuel Cell.

LOO Leave-One-Out.

NSGA Nondominated Sorting Genetic Algorithm.

NSGA-II Nondominated Sorting Genetic Algorithm II.

PCE Polynomial Chaos Expansion.

PDF Probability Density Function.

PEMFC Proton Exchange Membrane Fuel Cell.

SOFC Solide Oxide Fuel Cell.

Abstract

As the need for renewable energy to replace fossil fuels is getting more pressing, this transition is hindered as the erratic origins of renewables stand as a barrier to fully sustain the world's needs. To compensate for this natural imbalance, energy carriers such as hydrogen (H_2) carried through green ammonia seem to fit the role of the missing link to a sustainable green society. To convert these carriers back to electricity, existing technologies such as Combined Cycle Gas Turbines (CCGTs) have been studied. Novel technologies such as fuel cells, which allow to avoid exhaust fumes, are also alternatives. As the interest in the latter is rising, an optimisation and sensitivity analysis can be crucial to evaluate their capability in stationary applications. To assess this issue, I modelled a fuel cell power plant composed of an ammonia cracker, buffer tanks and a Proton Exchange Membrane Fuel Cell (PEMFC) stack. The model was tested to replace the imported load of a warehouse in Germany following their data in 2016. It was first submitted to a deterministic optimization through a Nondominated Sorting Genetic Algorithm II (NSGA-II) with 4 objectives: minimizing the PEMFC average over- and undershoots, the PEMFC transient response time, the buffer tanks mass content and power demand-production gap. Then, an uncertainty quantification was performed for several optimized designs with a Polynomial Chaos Expansion (PCE) algorithm. This report first presents a literature overview of both fuel cells and combined cycle gas turbine. It then exposes the model, its optimization and sensitivity analysis. It was found that minimizing the power over- and undershoot (8.63%) requires to increase the stack size (1499 cells) while minimizing both the transient response time (1.17 s) and the power demand-production gap (72 W/15min) is possible by decreasing the stack size (155 cells). The sensitivity analysis further revealed that the stack is highly sensitive to thermodynamical parameters defining its activation potential (76,1% to 93,4%), but also to its capacitance (83,4% to 91,6%) and to the power demand (64,1% to 92,1%). In conclusion, designs minimizing the PEMFC stack size are more flexible, while the system is still highly sensitive to thermodynamical parameters and to the power demand variation. Further researches including a dynamical description of the ammonia cracker and performing a robust optimization could help resolve the loopholes encountered in this study.

Chapter 1

Introduction

The last four decades have been a period of growing awareness of global warming and pollution. There is no doubt that most of world's population is now fully sensible of its influence on climate change. One of the key factor in Earth's warming is the emission of GreenHouse Gases (GHGs), the primary one being CO₂. To tackle this worldwide concern, countries have been gathering since the 80's to discuss GHGs' reduction goals and pathways [1]. A key field to achieve this emission reduction is the energy sector. Right now, world's energy demand mainly relies on fossil fuels (i.e. coal, petroleum and natural gas) [2], which are accountable for most of GHGs emissions [3].

An alternative path is to progressively drop our dependence on fossil fuels and shift to renewable energies such as solar and wind power. This shift is crucial given the coming depletion of fossil fuels. Yet this transition is still struggling to move forward as the exploitation of renewables poses some drawbacks. One of such drawbacks is the imbalance between the irregular availability of renewables and the energy demand. For example, solar energy infrastructures rely on the seasons, as excess electricity is often produced in summer but shortages happen during winter. A possible solution to this imbalance issue is the storage of energy surplus in energy carriers. This solution is commonly called the "Power-to-X" (PtX) pathway, with "X" referring to the energy carrier. This energy carrier can be used as a fuel when later needed in an "X-to-Power" pathway. This thesis focuses on this last pathway and more specifically "Ammonia-to-Hydrogen-to-Power".

Chapter 2

Ammonia

2.1 Why ammonia?

Around the 70-80's, scientists began to rely on hydrogen as one of the biggest alternative for future energy production. The use of hydrogen as an energy source began to be considered [4, 5], and kept on gaining interest in the early 21st century [6–9] until now. However, its implementation in the energy market remains restrained by several complications related to hydrogen containment, on-site production and transportation [10, 11]. These challenges have encouraged researchers to focus on hydrogen carriers such as organic methanol, formic acid, methylcyclohexane, ammonia and urea [3, 12–14]. The three first component are all Liquid Organic Hydrogen Carriers (LOHCs) [14] and thus have the major downside to be non carbon-free. Ammonia and urea therefore appear as greener carriers. Urea has the exclusive advantage of being both non-flammable and non-toxic, which is not the case of the other carriers. However, it is also one of the least hydrogen-dense component and hence will not be studied further [13]. This thesis focuses exclusively on ammonia, which features the following assets.

Above all, ammonia is a carbon-free chemical and thus will not directly emit CO_2 upon using it as a fuel, which makes it stand out from the rest of the hydrogen carrier aforementioned. However, when looking at its life cycle as a whole [15], ammonia is not entirely carbon-free given its production stage requiring the use of natural gas. Besides its carbon footprint, ammonia also has a nitrogen footprint in particular with its use in gas turbine leading to Nitrogen Oxide (NO_x) emissions, a type of GHGs. Nonetheless, ammonia synthesis is becoming greener thanks to carbon capture technologies - which applies well on ammonia synthesis [12, 16] - and renewable energy driven synthesis [17, 18].

A second asset of ammonia is its energy density. Ammonia - with its higher heating value (HHV) of 22.5 MJ/kg [19] and lower heating value (LHV) of 18.6 MJ/kg [20] - is one of the few materials, along with other hydrides [11], to show an energy density close to that of fossil fuels (around 20 MJ/kg for low-ranked coal and 55 MJ/kg for natural gas [21]). These energy density values are still far from the 120 MJ/kg LHV [20] and 142 MJ/kg HHV [19] of hydrogen, but ammonia has another asset. Its vapor pressure is at around 0.9 MPa, which is comparable to that of propane and makes it simple to store in inexpensive pressurised tank [22]. This property, combined with ammonia's hydrogen density at about 17.8%w [20], makes it possible to store it as a liquid with a volumetric density of hydrogen at around 108 g/L. That value is 45% higher than the 71 g/L of liquid hydrogen [12, 22], making liquid ammonia the liquid fuel with the highest volumetric hydrogen content (Figure 2.1) [23, 24]. When converted to volumetric energy density, liquid ammonia contains 15.6 MJ/L whereas liquid hydrogen holds 9.1 MJ/L and compressed gaseous hydrogen 5.6 MJ/L at 70 MPa [21].

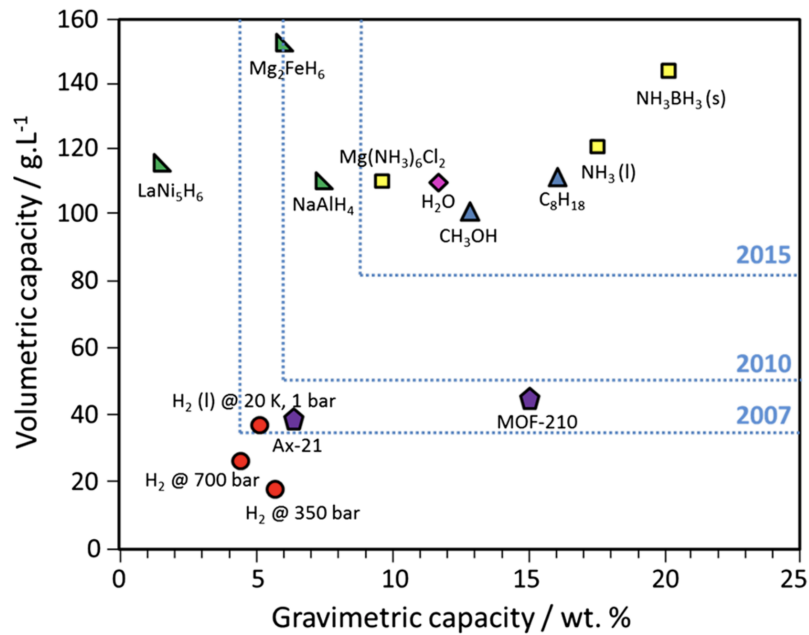


Figure 2.1: A graph of volumetric versus gravimetric hydrogen density for different hydrogen carriers. Circles represent hydrogen under different conditions; triangles represent hydrocarbons; pentagons represent materials for hydrogen physisorption; rectangles triangle represent metal hydrides; squares represent ammonia and related compounds. The dashed lines highlight the US Department of Energy targets for hydrogen storage. Extracted from [24]

One last benefit of using ammonia as a hydrogen carrier is the well-established infrastructure of the ammonia industry. Today roughly 180 million tons of ammonia are synthesized and transported each year [21]. NH_3 plays a role in numerous fields such as the agricultural and food sector (used as a fertilizer); the industrial sector (used as a refrigerant) and the chemical industry (used as an additive for selective catalytic reduction of NO_x) [25]. Historically, this Swiss Army Knife of chemicals reached a milestone at the beginning of the 20th century with the development of the Haber-Bosch process which consist of fixing atmospheric N_2 in the form of NH_3 . This innovation allowed the start of NH_3 mass production around 1913 [20]. As a consequence, both the agricultural and food sector witnessed an expansion which ultimately came into play in population growth [26]. In the end, this 100 years old industry is now entrenched with well-developed synthesis, storage and transport infrastructures thus drastically reducing the need of investment and the concerns in terms of safety issues [21].

Regarding these safety issues, ammonia is both a toxic and flammable substance. This last property is less concerning given the low reactivity of ammonia. Therefore, the risk of encountering an combustion or explosion situation is lower than other, more reactive fuels [21]. Ammonia toxicity however is more of a concern both to nature and human.

2.2 Production of ammonia

As written before, the ammonia sector is wide and old. Therefore, the ammonia production techniques are manifold. This section is focused on the most common process (i.e. Haber-Bosch) and the electrochemical ammonia synthesis.

2.2.1 Haber-Bosch process

The Haber-Bosch process developed in the early 20th century was introduced earlier as the milestone of ammonia industry, allowing the ammonia production to skyrocket. It remains the most common synthesis technique used worldwide. This process consists in the fixation of atmospheric N_2 to H_2 (Equation 2.1). This exothermic reaction takes place in a iron-based catalytic reactor which works at optimal temperature and pressure between 350-500 °C and 150-250 bar. The total conversion in commercial reactors lies between 20 and 30% [27,28].



Regarding the feedstocks, nitrogen is obtained from air separation, the most efficient and cost-effective technique being cryogenic air separation [29]. Hydrogen produc-

tion has several alternatives: Steam Methane Reforming (SMR), coal gasification and partial oxidation of heavy fuel oils [28, 30]. In 2012, hydrogen from SMR accounted for more than two-thirds of the ammonia production [31, 32]. However, coal gasification remains predominant in some countries like China given their abundant coal resources [30]. The hydrogen production techniques aforementioned rely on fossil fuels, thus sources of GHGs. On a worldwide scale, the ammonia production sector is responsible for approximately 0.93% of all GHGs emissions, as 1 ton of produced ammonia emits around 2-3 tons of carbon dioxide [33]. Hence, in an era of sustainable development and emissions mitigation, greener H_2 production alternatives are in sight such as electrolysis and biomass gasification [17, 18, 34–36].

2.2.2 Electrochemical ammonia synthesis

The Haber-Bosch process still poses issues of low conversion and high operating conditions. Recent researches are aiming at finding less energy-intensive and more efficient alternatives such as the electrochemical production of ammonia with the most promising methods being Solid State Ammonia Synthesis (SSAS), where ammonia is produced electrochemically in an electrolyzer cell through a dense solid electrolyte based either on a ceramic or a polymer material [37–39]. Although SSAS is still a premature technology, it is predicted to save more than 20% of the current energy consumption [40, 41].

Chapter 3

How to unleash the power of ammonia

When addressing the topic of renewable energies, one aspect that often comes back in the discussions is the problem of intermittent electricity production. This is due to the unpredictable behaviour of the natural resources they rely on [42,43]. Together with this fluctuating supply, the energy demand also varies daily and seasonally [44]. In response to these challenges, engineers have been focusing their researches on technologies that could allow the storage of energy [45]. Such technologies are based either on electrical, mechanical, thermal or chemical storage [44]. Ammonia-to-Power falls under this last form. Once the energy is stored under carriers such as ammonia, the question is: what are the possible ways to revert these carriers back to electricity? The main studied techniques to answer this question are: the integration of ammonia as a working fluid in power cycles, its combustion for transportation in vehicular motors and propulsion reactors, its use as a fuel in fuel cells or in combined cycle gas turbines [21]. The last two alternatives are the ones at the center of this thesis.

This section first details the working principle of both fuel cells and combined cycle gas turbines before comparing both technologies in terms of conversion to hydrogen, flexibility, limits and design uncertainties. In the end, a decision is made on which one of the system is going to be studied.

3.1 Fuel cells

Fuel cells (FCs) are static energy conversion installations based on the conversion of chemical to electrical energy through the reaction of a fuel and an oxidant with no intermediate mechanical conversion. In terms of general design, one cell is composed of an anode, an electrolyte and a cathode, the electrolyte separating both

electrodes. Typically, the fuel is fed into the anode while the oxidant is fed into the cathode. There, two scenarios are possible given the type of ion mobility specific to the electrolyte: either the oxidant turns into anions, or the fuel gets decomposed into electrons and protons. In either case, the ions are transported through the electrolyte and react with the oxidant or the fuel, generating byproducts (water and heat). A current is created in the circuit connecting both electrodes as electrons are generated following the fuel reaction with the oxidant [46, 47]. A schematic of a generic fuel cell is shown at Figure 3.1.

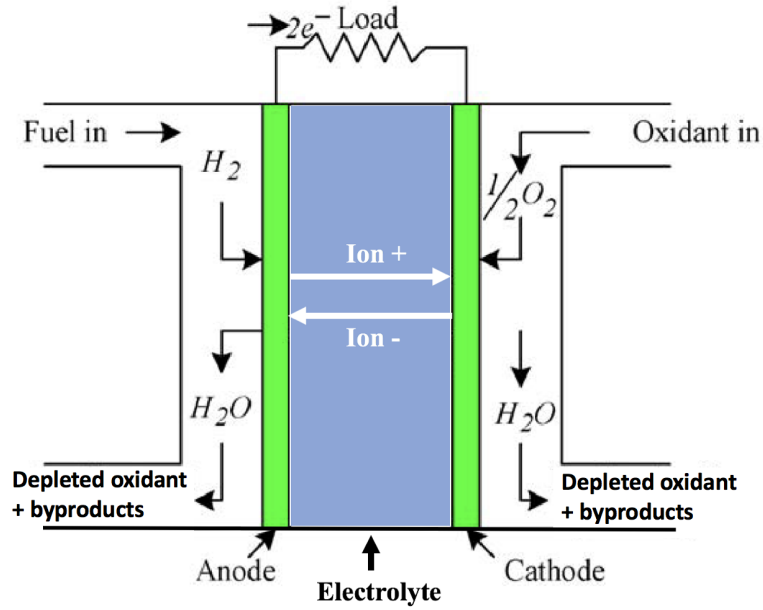


Figure 3.1: A fuel cell installation diagram: the electrodes are shown in green, the electrolyte in blue and the ion path in white (modified from [46]).

Since the invention of the first Fuel Cell (FC) nearly two centuries ago, several types have been developed. It is common to classify those numerous form of cells as a function of their electrolytes and the fuel they run on. Five main categories are generally considered: alkaline, molten carbonate, solide oxide, proton exchange membrane and phosphoric acid [46, 48]. The potential fuel cells for an Ammonia-to-Power application were narrowed down to Alkaline Fuel Cell (AFC), Solide Oxide Fuel Cell (SOFC) and PEMFC, as they seem to be the most commonly used for this application [21, 49, 50].

3.1.1 Alkaline fuel cells

Alkaline Fuel Cells (AFCs) were one of the first ammonia fuel cell system to be developed in the 1960's [51]. An AFC is based on an alkaline: a liquid such as aqueous solutions of potassium hydroxide (KOH) or molten hydroxide eutectic mixtures of KOH & NaOH; or a solid such as membranes in Alkaline Membrane Fuel Cells (AMFCs) [49, 50]. The membrane in AMFCs can be made of an anion-exchange resin layed on polyvinyl alcohol (AER-PVA). Regarding the electrodes, many materials can be used such as nickel, ruthenium, iron, platinum [49].

Ammonia AFCs can be fed indirectly with hydrogen from cracked NH_3 but also directly with NH_3 . The latter feeding method is getting more and more under interest as it could avoid the use of an external cracker unit [52, 53]. Moreover, indirect ammonia AFCs were proven tolerant to ammonia, contrarily to PEMFCs [54, 55]. Regarding the working temperatures, aqueous AFCs present a working temperature of 50 to 200 °C [51]. Molten hydroxide fuel cells operate at higher temperatures of 200 to 450 °C [56] whereas AMFCs can be used at room temperature (25 °C) [57]. Finally, AFCs' efficiencies lie between 60 and 70% [46].

A general flow diagram for an aqueous AFC diagram is shown on Figure 3.2.

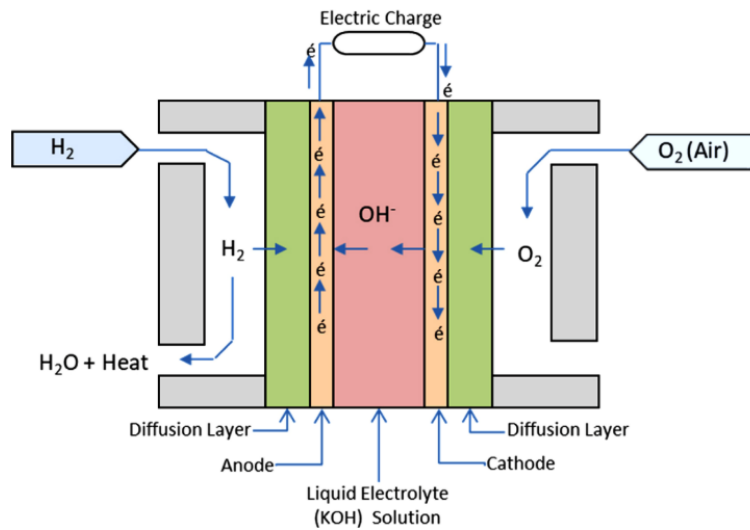


Figure 3.2: Diagram of a hydrogen-fed aqueous AFC (retrieved from [58])

AFCs are already developing on a worldwide scale. Project Alkammonia is one leading company for AFCs technology in Europe [59]. In 2015, an english company named AFCenergy - the only AFC company still active [60] - successfully operated a 101-cells stack providing 240 kW AFCs system in Germany. It developed the project further in 2018 with a 1 MW system [61, 62]. AFCenergy also signed a

project for a 50 MW FC power plant in Daesan (Korea) [63]. A third FCs company named GenCell launched 800 4kW AFCs in Kenya [64].

3.1.2 Solid oxide fuel cells

Solid Oxide Fuel Cells (SOFCs) are characterised by a solid electrolyte (usually a ceramic) and a high operating temperature [46]. There are two types of SOFCs, based on the ion that gets transported through the electrolyte: SOFC-H and SOFC-O (Figure 3.3) [21]. SOFC-H use proton-conducting electrolytes (such as barium cerate); whereas SOFC-O use oxygen-ion-conducting electrolyte such as Yttria Stabilized Zirconia (YSZ) [65]. The anode is usually nickel-based cermets like Ni-YSZ or Ni-GDC [66,67]. The cathode is usually LSCF or BSCF [52,67,68]. Figure 3.3 shows a cracking reaction at the ammonia inlet, highlighting that SOFCs can be directly fed with ammonia that gets cracked as soon as it encounters the anode [52]. Regarding working temperatures, SOFCs work at high temperatures that vary between 500°C and 1000°C approximately [48,69]. Finally, SOFCs have efficiency values between 50-60% [21,46,70].

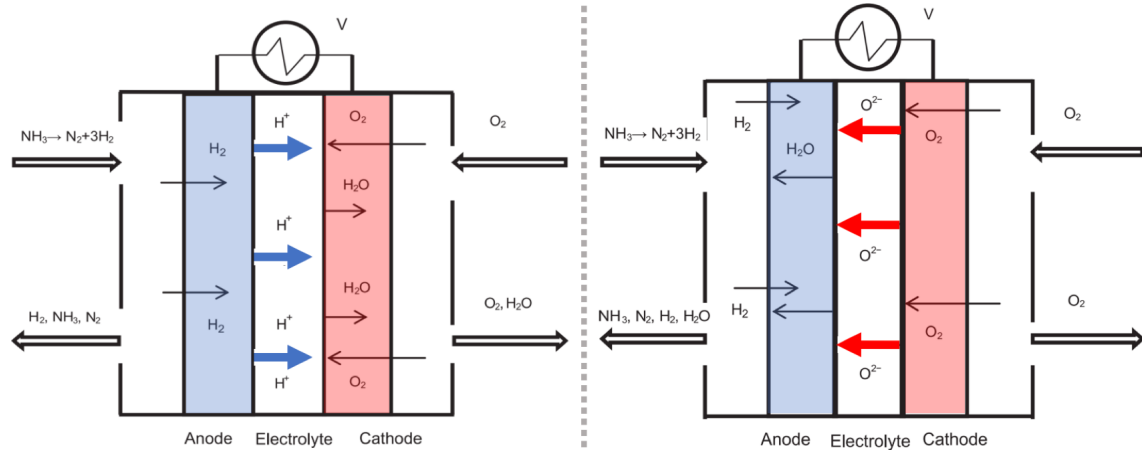


Figure 3.3: Diagrams of the two types of SOFC, namely (from left to right): a proton-conducting SOFC; an oxygen ion-conducting SOFC. The proton and oxygen-ion exchange direction are shown in blue and red respectively (modified from [49]).

When it comes to the latest commercial SOFCs applications, the Japanese company IHI reportedly launched a 1 kW ammonia-fed SOFC in 2018. The company announced that they would continue to enlarge their system for future industrial applications [71].

3.1.3 Proton exchange membrane fuel cells

Proton Exchange Membrane Fuel Cells (PEMFCs) have the particularity to have a solid polymeric membrane electrolyte (Figure 3.4) [72]. The membrane electrolyte are usually made of Nafion or Teflon [46]. PEMFCs do not work on direct ammonia feed. In fact, it has been demonstrated that the presence of ammonia, as low as 1 ppm, is responsible for permanent contamination damages on both the membrane and the anode [73,74]. As a consequence, PEMFCs only operate with a $>99.5\%$ pure hydrogen feed from cracked ammonia [75]. Such high decomposition degrees in ammonia cracker reactors were studied on several different metal catalysts such as Ni, Ru, Ir, Pd, Pt, Rh and NaNH_2 [75–80]. In 2019, a detailed review of the performance of reported catalysts was published by Alboshmina et al. [81]. PEMFCs are low temperature fuel cells. They typically operate between 60°C and 120°C [48,82]. Past that threshold, the membrane dries out and loses conductivity [83]. Finally, PEMFCs have known efficiencies in the range of 35-45% [46,70].

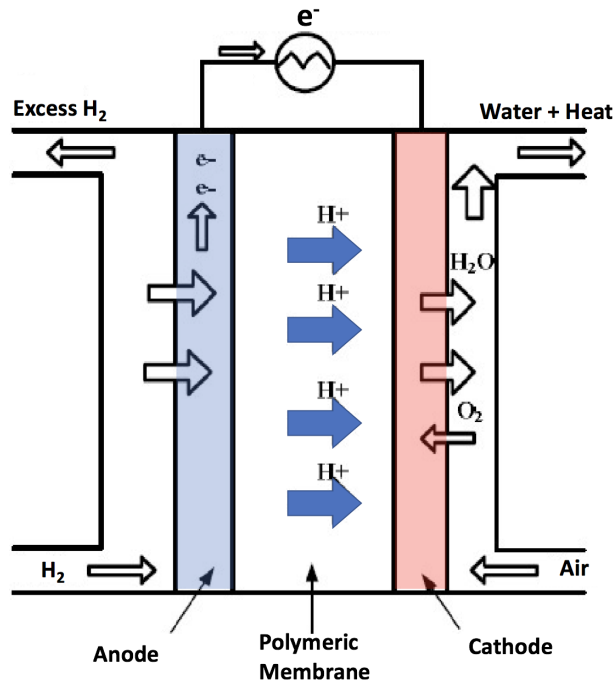


Figure 3.4: PEMFC diagram: the anode is shown in blue, the cathode is shown in red, the proton exchange direction is shown with blue arrows (modified from [84]).

When it comes to stationary industrial applications, the dutch PEMFCs company Nedstack successfully installed world's first 2 MW PEMFC power plant for the fine chemicals group Ynnovate in Yingkou, China [62,85]. This breakthrough took place in 2016, seven years after the installation of their first 1 MW PEMFC plant

in Solvay, Belgium.

3.1.4 Assets and challenges

Concerning their assets, AFCs are tolerant to ammonia, their operating temperatures are not as high as for SOFCs and they show the highest efficiency ranges of all three FCs discussed.

AFCs also have to meet four challenges that could hinder their application and performances. The first one is the expensive treatment of the electrolyte that requires to be purged from the water produced in the reaction [60]. The second challenge is the performance degradation following the electrode corrosion but also the presence of CO_2 in the cells. Corrosion by the electrolyte ultimately reduces an AFC lifetime to orders of 15000 hours, which is deemed unacceptable for stationary application [60]; while the CO_2 -pollution can be treated by purifying the air stream beforehand. Both these corrosion and pollution issues can also be avoided if AMFCs are used [52, 60]. A third challenge is the corrosive nature of electrolytes (KOH, NaOH) [83]. Lastly, the cost of the metal used for the electrodes can be high depending on its value and scarcity [83].

SOFCs permit direct ammonia feed without contamination concerns, with an efficient heat recovery and durable solid electrolytes [83]. Moreover, the SOFCs high operating temperatures allow their use on large scales and in combined heat and power co-generation plants [46, 86].

As SOFCs are operating at high temperatures, their biggest challenges concern longevity, thermal expansion of the materials but also stability [87]. A second challenge occurring with SOFC-H is a phenomenon of hydrogen dilution in undecomposed ammonia and nitrogen at the anode, leading to performance losses. Therefore, the theoretical observation that SOFC-H are more efficient than SOFC-O is often not met in reality [52, 67, 87, 88].

PEMFCs operate at conditions close to room temperatures, which allows small scale mobile applications (not the case of this thesis) [21]. A second asset of PEMFCs is their almost immediate start-up and response times, making them the most responsive type of cell.

However, PEMFCs have multiple drawbacks such as the cost of the precious metal electrodes [83] and their intolerance to components such as ammonia and CO , which can contaminate the polymer membrane even at very low quantities (1ppm for ammonia) [46, 74]. Moreover, PEMFCs tend to have slightly lower efficiencies (35-45%) compared to AFCs and SOFCs [46, 70].

3.2 Combined cycle gas turbine

3.2.1 Working principle

The concept of CCGT plant can be summarised in three different functional blocks: a combustion chamber, a gas turbine (Figure 3.5) and a heat exchanger. In chronological order, the air feed first gets compressed in a compressor then meets the fuel supply which is burnt in a combustion chamber to form a hot compressed mixture. Then, this air-fuel mixture is sent through the turbine blades, which rotates and powers an alternator to produce the main electric supply. When leaving the gas turbine, the exhaust gas is retrieved and injected in a heat exchanger. There, the exhaust gas has two alternatives. It either generates steam which in turn produces electricity through a steam turbine; or it is used as a heating source [89].

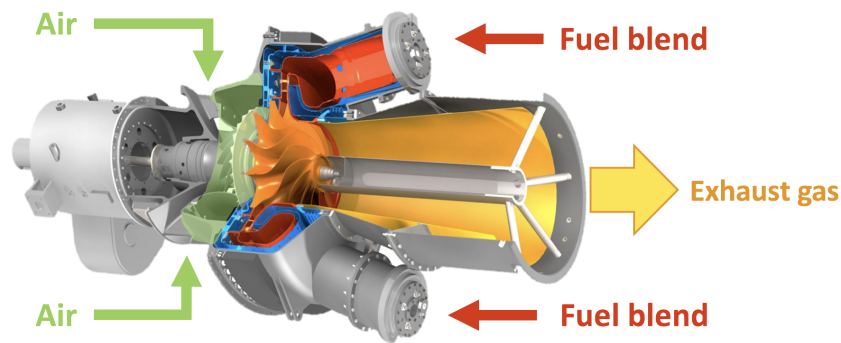


Figure 3.5: Schematic of a gas turbine. The combustion chamber is highlighted in red; the air compressor in green; the turbine blades in orange and the exhaust gas diffuser in yellow (modified from [90]).

3.2.2 Integration of ammonia as a fuel

Nowadays, CCGT are fuelled mainly by hydrocarbons such as diesel, gasoline and natural gas [36, 41]. Ammonia and hydrogen have been studied to replace these polluting fossil fuels in CCGT. The question now lies in the integration of ammonia as a CCGT fuel. Two scenarios are possible: using a pure ammonia feed or using blends of ammonia and another fuel.

Right now, researchers have shown little interest in the scenario of pure ammonia-fed CCGT. In fact, in the earliest studies conducted on ammonia combustion properties in the 1960's [91–93], researchers have demonstrated that pure ammonia's combustion properties were unfavorable compared to fossil fuels for several reasons. First of all, ammonia's low reactivity leads to minimum ignition energy

higher than for fossil fuels (16 times the value of propane). In terms of auto ignition temperature, this translates to 651 °C for ammonia compared to 256 °C for diesel [36]. Finally, the range of equivalence ratios (e.g. the ratio between the actual and the stoichiometric air/fuel proportion [94]) at which the pure ammonia flame is stable turned out to be narrower than for hydrocarbon fuel flame. In the end, Verkamp et al. concluded that the alternative of using ammonia blended with another component (in their case: 28% of hydrogen from ammonia decomposition) could bring these three properties to the ideal range of fossil fuels. More recently, other issues such as slow burning velocity of pure ammonia and high amounts of NO_x emissions allowed to undermine the first scenario and favour the ammonia-hydrogen blend scenario [95, 96].

The second scenario (ammonia blends) appears to be the best. Such blends can be ammonia-methane [97, 98]; ammonia-kerosene such as in the Japanese 50kW micro-gas turbine prototype [99]; or ammonia-hydrogen [91, 100, 101]. However, the blend alternative is not perfect either. For example, the narrow equivalence ratio issue such as reported by Verkamp et al. [91] persists with blends [102]. One last note is that the ammonia-hydrocarbons blends won't be reviewed here, in the intent to stay focus on the ecological carbon-free goal of this research.

3.2.3 Existing projects

Regarding existing ammonia related CCGT projects, there are numerous. In Japan, a 155 MW coal-fired plant was tested with co-fired ammonia in Mizushima by Chugoku Electric Power Company [21]. There is also a 50 kW ammonia-kerosene plant in Fukushima owned by FREA [99]. In USA, SPG had commercialisation plan in Montana [41]. In the Netherlands, NUON plans a two-step adaptation to run CCGT on ammonia in Eemshaven. The first step is to convert a CCGT to co-fire 10% ammonia in 2021. The second step is to reach 100% ammonia firing in 2026 [103].

3.2.4 Assets and challenges

Using ammonia as a CCGT fuel offers some assets compared to other traditional fuels. The first one is quite obvious: ammonia is carbon-free and thus environmental-friendly. The second one is that ammonia, compared to fossil fuels, needs to be injected at higher mass flow rate but produces the same amount of work at lower temperatures. This can be explain by the lower LHV of ammonia compared to fossil fuels. This decrease in operating temperatures allows a longer pause between two maintenance checks but also means that, for the same outlet temperature, an ammonia-fed CCGT would yield 10 to 20% more power than a hydrocarbon-fed

CCGT [41].

Regarding the challenges, companies and researchers such as SPG Advanced Propulsion and Energy [21,41,100] or Yapicoglu et al. [36] have exposed the major obstacles that still need to be overcome: The slow flame kinetics leads to blowoff and high emission at the combustion start-up; the combustion of ammonia is unstable; an enhanced ammonia vaporization system is needed to improve efficiency; the turbine is subject to corrosion; an appropriate cooling system is required and last but not least: NH_3 combustion is responsible for NO_x emissions.

Solutions to these challenges already exist or are being studied. Regarding the slow combustion kinetics, Li et al. demonstrated that the addition of hydrogen in an ammonia-hydrogen blend can improve the NH_3 burning velocity [95]. The unstable combustion could be stabilised with a tangential swirl burner [97,100]. The corrosion can be avoided by replacing the turbine sensitive pieces with non-corrosive materials [36]. Finally, the NO_x emissions issue can be dealt in different ways. A first and straightforward solution is to post-treat the exhaust gas through Selective Catalytic Reduction (SCR) [98]. A second one consists in working with an ammonia-rich blend [95,104] but this conflicts with the slow flame kinetics solution aforementioned. Therefore, a trade-off should be found. A third alternative is the use of a swirl burner. Finally, a fourth amelioration could be to increase the equivalence ratio or the pressure [21].

3.3 Comparison

It is a fact, gas turbines are more mature than the recently expending fuel cells. However, this does not necessarily mean that CCGT is the best alternative for Ammonia-to-Power. The discussion between combustion and fuel cell technologies was already initiated in 1998 by Ulleberg with a paper in which he chose to focus on fuel cell after exposing that highest overall conversion efficiencies can be achieved by fuel cells compared to combustion engines [86]. In this report however, the choice is not that straightforward, as several elements are at stake. This section focuses on the comparison between both technologies in terms of assets and challenges, hydrogen processing methods, flexibility, limits as well as design uncertainties. As for fuel cells, a distinction is made once again between AFCs, SOFCs and PEMFCs. In the end, a choice is made considering all the discussed parameters.

3.3.1 Hydrogen processing

Fuel cells

This study will focus only on indirect ammonia fuel cells, meaning the cell is fed with hydrogen coming from an ammonia cracker with ammonia playing the role of hydrogen carrier. As mentioned before, both AFCs and SOFCs could work as direct ammonia fuel cells. This alternative has been at the center of researches for the last decade [53, 57, 68, 105]. However, it has been proven that direct ammonia fuel cells had lower performances than hydrogen-fed fuel cells [68, 106]. Besides, PEMFCs are intolerant to ammonia as it is poisonous for the membrane.

Combined cycle gas turbine

As explained before, two fuelling modes are being studied for combined cycle gas turbine: pure ammonia or ammonia and hydrogen blend. Both alternatives have been compared in a previous discussion in which the pure ammonia alternative was ruled out. Therefore, the turbine would be fed with a partially cracked ammonia mixture containing both ammonia and hydrogen in a stable enough ratio considering the challenges aforementioned.

3.3.2 Flexibility

When assessing flexibility, one aspect that is important is the technology's dynamic behaviour in the electrical grid: How long does it take for the system to start-up ? How fast can it compensate for demand variations (i.e. ramp-up rates)?

Fuel cells

A first factor to take into account is the start-up time of each fuel cell system. PEMFCs are said to have an almost immediate start-up. AFCs have a fast start-up on the scale of minutes. SOFCs have the longest start-up of all FCs: up to several hours depending on the size of the stack [58, 107].

Regarding the ramp rates, the scales are similar: PEMFCs respond almost immediately, AFCs respond in a matter of second while SOFCs have a response time on the scale of hours. More precisely, Nikiforow et al. assessed the ramp rates of a 5 kW PEMFC with a 53% to 90% power ramp ranging from 0.1 to 1 s depending on the stoichiometry [108]. Staffell et al. gathered information from a Japanese small scale SOFCs system having a ramp rate of 0.7% of the power capacity per second, enabling them to tolerate power variations of 300 W/min. As no AFCs

ramp rates data could be found, an extrapolation can be made based on alkaline electrolyzers showing ramp rates between 0.2%/s and 20%/s [109]. The same comparison can be drawn between PEMFCs and PEM electrolyzers, confirming the values aforementioned [110].

While they have the fastest start-up and response times, PEMFCs are intolerant to ammonia. Considering they need a certain feed purity to avoid ammonia contamination, this should be taken into account as a time margin on the cracker for the fuel feed to reach >99.5% is thus needed [75].

Combined cycle gas turbine

According to the International Renewable Energy Agency, CCGT plants show start-up times ranging between 1 and 4 hours [111]. In their 2019 study on the impact of renewable energies intermittence on CCGT's emissions, Blondeau et al. confirmed the distinction between cold and hot start-up conditions assessed by Rossi et al. two years prior. Both studies observed that cold start-ups take around 2 hours and hot start-up take less than 1 hour [112, 113]. When looking in more details at technical specifications of GE and Siemens turbines, both their start-ups take around 30 minutes [114–116].

In their 2019 technical article, the Finnish company Wärtsilä reported that the ramp rates of CCGTs are limited by the materials composing the heat recovery unit and the steam turbine. Therefore, the gas turbine itself is constrained to holding points in order for the steam to rise slowly in temperature and pressure. Most ramp rates range between 10 and 100 MW/min, with an average of 25 MW/min [117]. Once again, more precise data can be found on technical specifications of GE and Siemens products. The GE 7ha turbine ramps up at a rate of 55 to 75 MW/min [116]. The Siemens SGT6-5000F turbines ramps up at 40 MW/min [118].

3.3.3 Limits

Fuel cells

The working temperatures for each fuel cells have been listed earlier. Here is a more comprehensive description of each FCs characteristics and operating conditions. AFCs work between 50-200°C and 1-5 bar at efficiencies ranging between 60 and 70% [46, 51]. SOFCs work between 500-1000 °C and 1-10 bars with 50 to 60% efficiencies [46, 48]. PEMFCs work between 60-120 °C and 1-3 bars. This low-temperature condition is a crucial limit to control for the membrane to remain

wet and avoid damage due to drying [48, 82, 83].

Regarding the size of an FC installation, a unique cell generally has a potential of around 0.7 V. To obtain a consistent power output for larger scale applications, several cells must be arranged in stacks [119]. In addition to that, a characteristic of FC stacks is that their efficiencies are unaffected by their size, meaning they can be broken down into several smaller stacks arranged in parallel and still have the same efficiency, thus avoiding size limitations [86, 120].

Combined cycle gas turbine

Regarding CCGTs operating parameters limits, the maximum turbine inlet temperature is fixed by the turbine materials while the maximum turbine inlet pressure is determined by the compressor and its efficiency. The maximum CCGTs efficiency is itself linked to the turbine inlet temperature. In 2013, Mitsubishi Heavy Industries (MHI) released a technical report gathering their breakthroughs in enhancing CCGTs efficiencies through the increase of the turbine inlet temperature. Starting from 1150°C in the 1980s, MHI is now able to reach the world's record of 1600°C, with a compressor working at a high pressure ratio of 25 allowing a thermal efficiency of 61.5% or more [121]. Other gas turbine models such as the GE 7ha or the Siemens SGT6-5000F respectively work at a net cycle efficiency of 63-64% and 59.7% [116, 118]. Regarding existing ammonia-fed CCGTs studies, Bozo et al. newly modelled a CCGT fed with a 30/70 hydrogen-ammonia blend at an inlet temperature of 987°C and a compressor ratio of 10.2 [122].

When assessing CCGT limits, both the fuel blend ratio and the equivalence ratio are critical factor to ensure the combustion stability. On the one hand, there is the fuel blend ratio: ammonia-rich blends show slow burning kinetics leading to ignition difficulty and high emissions during start-ups while hydrogen-rich blends emit more NOx [36, 100]. In 1967, Verkamp et al. concluded a 28-72 vol.% hydrogen-ammonia blend would be optimal [91]. This ratio is still used nowadays in research papers [122]. On the other hand, the equivalence ratio (Φ) is limiting as it determines the stability region of the flame velocity and thus the combustion. It also plays a role on the NOx emission. Nozari et al. concluded that high equivalence ratio (e.g. high fuel content) lead to a wider stability region. Moreover, they measured for a 80/20 ammonia-hydrogen blend that negligible NOx emissions were reached starting at $\Phi = 1.1$ and maximum NOx emissions at around $\Phi = 0.6$ [101, 104].

3.4 Conclusion

After an introduction on Ammonia-to-Power, fuel cells and combined cycle gas turbines, followed by a comparison between both technologies, I was able to make a choice on which one I wanted to use for my model. I chose to work with fuel cells for the following reasons.

The main reason that drove me to make that choice is the relative novelty of this technology. At first sight, the reader could think of it as a drawback, seeing fuel cells as immature. I personally think of it as a promising technology, evolving each year. In addition, FCs do not have the burden of combustion exhaust gases such as NOx, unlike gas turbine. This last point is all the more crucial given the emissions reduction goals that are at stake in the climate issue. A second reason I chose FCs is their "convenience", in a sense that they can be built and replaced piece by piece, as one FC unit is stackable. This allows a certain scale flexibility to adapt to several power demand scenarios.

In the end, a type of fuel cell had to be chosen from the three types exposed before. As it has the biggest value of start-up times and ramp rates, SOFCs were ruled out right away, being the least susceptible to sustain grid variations. AFCs were also ruled out for several reasons, the first one being the lack of recent industrial project. This is most certainly due to the disappearance of all industrial AFC company but one (AFC Energy PLC). The decreasing interest can be explained by the numerous challenges that AFC still poses including its high footprint which goes against the eco-friendly character of Ammonia-to-Power [60,123]. Ultimately, PEMFCs were chosen for this model for several reasons. On the one hand, PEMFCs have the fastest start-up and response time, providing the system with the most flexibility regarding grid variations balancing. On the other hand, PEMFCs seem to have gained the most interest in research as hundreds of models are already listed and being programmed [124,125]. PEMFCs were already being preferred to AFCs in 1998 [86]. Considering the drawbacks mentioned earlier, they are not insurmountable: the ammonia poisoning is manageable with high-efficiency cracking and ammonia scrubbers and the low temperature requirements can be dealt with cooling. Besides, recent improvements are emerging such as High-Temperature Proton Exchange Membrane Fuel Cell (HT-PEMFC), studied by Cinti et al. in 2020 by replacing the commonly used Nafion membranes with PBI membranes [126]. In the following chapters, I will first expose the fuel cell stationary plant I modelled, followed by the robust design optimization applied on that model where the polynomial chaos expansion technique is coupled to the NSGA-II algorithm. OR The thesis is organized as follows: Chapter 2 through 4 introduced the problematic of Ammonia-to-Power through the comparison between CCGTs and FCs; Chapter 5 presents the methodology; Chapter 6 presents the results and discussion.

Chapter 4

Methodology

This chapter describes the methodology starting from the modelling of the whole Ammonia-to-Power system to the working principle of the optimization and uncertainty quantification of that system. At first, the overall system is presented graphically. Then, the system is broken into blocks to highlight each model used, together with their main equations. Finally, the working principle of the optimization and uncertainty quantification framework is detailed.

4.1 System model

The ammonia is first fed into a reactor made up of two parts: an ammonia cracker and a combustion reactor (Figure 4.1). In the cracker, the ammonia is decomposed into hydrogen (H_2) and nitrogen (N_2) in an endothermic catalytic reaction driven by the heat provided by the combustion reactor. The outlet feed is a gaseous mix of N_2 and H_2 with traces of NH_3 . This feed goes through a NH_3 removal system to get rid of the ammonia residue before being fed into the ammonia-intolerant fuel cells. Ammonia removal can be performed with various technologies such as scrubbers [127], membrane separators [128], dynamic adsorption [129]. The purified N_2/H_2 feed is then stored in buffer tanks which are needed to handle peak variations in electricity demand (as the flow rates in the cracker and in the PEMFC are not identical). When feeding the PEMFC stack, the H_2/N_2 mixture enters at the anode side. The nitrogen could get separated from the feed as it is useless but it actually has negligible influence on the reaction, as demonstrated by Cinti et al. [126]. Technologies such as Pressure Swing Adsorption (PSA) allow to separate N_2 from the H_2 stream [130]. The fuel cell oxidant feed is ambient air and is fed at the cathode side. As PEMFCs operate at low temperatures, they are generally coupled to a cooling system using either liquid or air as a cooling fluid [120]. When the conditions are suitable, the stack produces direct current

which then can be converted to the grid's requirement through DC/AC or DC/DC converters [131]. It is important to note that Figure 4.1 does not show any heat exchangers or compressors. In a real system, heat exchangers are needed between the high-temperature cracker and the NH_3 removal, between the buffer tanks and the low-temperature PEMFC stack and inside the PEMFC installation itself to keep it to a the operating range of 60 °C to 120 °C. Moreover, as the buffer tanks are storing at a pressure of 300 bar, a compressor is needed between the NH_3 removal and the buffer tanks [132]. To have an indication on the order of magnitude, the energy required to compress hydrogen from 20 bar to 350 bar is 1.05 $\text{kWh/kg}_{\text{H}_2}$ [133].

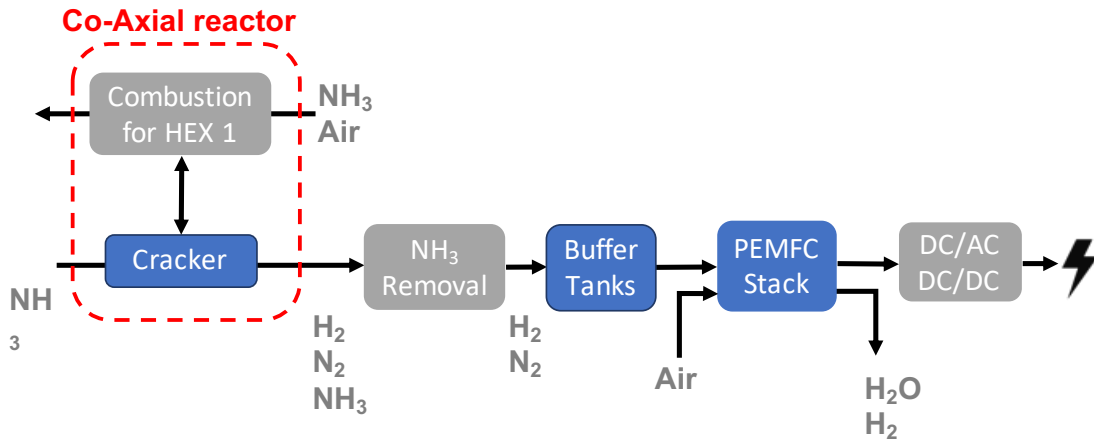


Figure 4.1: A graphical representation of the ammonia-to-power installation to be studied. Blue blocks represent the modelled parts while grey blocks show the non-modelled but necessary additional components. The black arrows give the general direction and order of the processes.

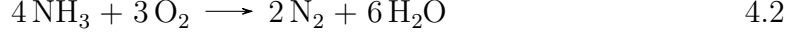
4.1.1 Ammonia cracker

The first modelled block of the system is the ammonia cracker. Two cracking mechanisms are possible: thermal or catalytic [81]. In this model, the cracking is catalytic and takes place in a cylindrical packed-bed reactor filled with metal catalyst particles. The ammonia undergoes a decomposition reaction throughout the bed (Equation 4.1).



The reaction is endothermic and requires an enthalpy of $-46 \text{ kJ/mol}_{\text{NH}_3}$ [12]. This energy is supplied by heat exchange with a combustion reactor in which ammonia

is burned (Equation 4.2) [20]. The combustion can also take place with other fuels such as hydrogen [128].



Regarding the design of catalytic reactors, literature shows several possible infrastructures such as packed bed microreactors [134, 135], microchannel reactors [136, 137], monolithic reactors [138], membrane reactors [139] and electrochemical reactors [140, 141]. For this study, a cylindrical packed-bed configuration was chosen following Chein et al. 2010 study. Regarding the combustion needed to heat up the cracker, the reactor is assumed to have a concentric-tube configuration such that the combustion takes place in the outer shell, while the cracking takes place in the inner tube (Figure 4.2). Such a configuration allows a compact design and has already been studied in the context of PEM fuel cell installations [128, 142]. Regarding the flow configuration, the reactor can operate in cocurrent [128] or in counter-current [142], the latter being preferred for an improved heat exchange. It is further assumed that the heat exchange between the cracker and the combustor is ideal, therefore always delivering enough heat for the cracking to take place. The combustor is thus ignored in the modelling.

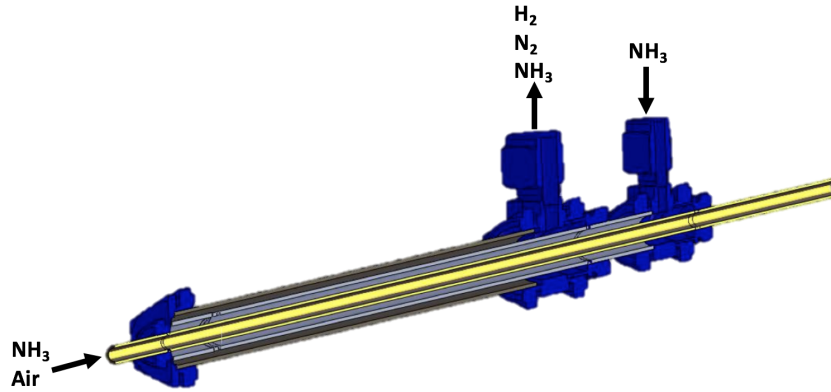


Figure 4.2: A 3D schematic of a concentric-tube ammonia cracking-combustion reactor composed of (from inner to outer layers): the feed valves (blue), the combustion cylinder (yellow), the cracking cylinder (light grey) and the cracking product cylinder (dark grey). Modified from [142].

Choice of catalyst

The catalyst used in the model is based on the study of Chellappa et al. where a nickel catalyst was chosen [75], even though ruthenium or iridium-based catalysts are both more efficient [79]. However, when we consider economics, both

ruthenium and iridium - as well as other commonly studied catalyst metals such as platinum, rhodium and palladium [77] - are rare and thus expensive metals. Moreover, the activity of nickel was shown to be close to iridium and ruthenium high performances when operating at higher temperatures [76]. Therefore, when taking both efficiency and cost into account, nickel appears to be the best and most economically viable alternative. Its performances can even be improved to decomposition efficiencies values up to 99.90% thanks to the addition of cerium oxide (CeO_2). This addition enlarges the catalyst pores which optimises the reaction [81, 138, 143]. In the adopted model, the nickel particles are mixed with platinum which acts as a stabiliser to prevent the sintering of the reaction sites. The Ni-Pt mixture is deposited on an aluminum oxide support (Al_2O_3) [75].

Decomposition kinetical model

The decomposition mechanism is modelled as a first order reaction, following the Langmuir-Hinshelwood approach. For this assumption to be true and the first-order model to show robust predictions, both the operating temperatures and the ammonia concentration need to be high. Therefore, the valid range of operating temperatures T_c is between 813.15 and 893.15 K, while the valid range of ammonia concentration is met with an inlet pressure p_{in} between 1 and 2 bar [75, 134].

The resulting reaction rate expression corresponding to NH_3 first-order cracking on Ni-Pt/ Al_2O_3 catalysts is an Arrhenius equation (Equation 4.3).

$$r_0 = kp_{\text{NH}_3} = Ae^{\left(\frac{-E}{RT_c}\right)}p_{\text{NH}_3} \quad [\text{mol}_{\text{NH}_3}/\text{g}_{\text{cat}}h] \quad 4.3$$

The rate thus depends solely on the ammonia partial pressure p_{NH_3} [bar]. k is the rate constant expressed in $[\text{mol}_{\text{NH}_3}/\text{g}_{\text{cat}}h\text{bar}]$. The latter gathers the pre-exponential factor A and the activation energy E . According to Chellappa et al. A has a value of $3.639 \cdot 10^{11}$ $[\text{mol}_{\text{NH}_3}/\text{g}_{\text{cat}}h\text{bar}]$ and E has a value of 46.897 $[\text{kcal}/\text{mol}_{\text{NH}_3}]$ [75].

Chein et al. proposed an extension of the rate expression following the rate of Methanol-Steam Reforming (MSR) in a bed packed with $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalysts as both process are deemed similar. An adaptation of the rate reaction (Equation 4.4) allows us to include the catalysts dimensions (through the catalyst porosity ϵ), their effectiveness and activity (through the correction factor C_R). Furthermore, this adapted expression enables us indirectly to include the reactor dimensions through the catalyst bed density ρ_b . This density can be expressed as the ratio of the mass W and the volume V_b occupied by the catalyst. As $V_b = \pi R_b^2 L_b$, the radius R_b [m] and the length L_b [m] of the bed can be assumed close to the radius R_r and the length L_r of the reactor itself.

$$r = C_R(1 - \epsilon)\rho_b r_0 = C_R(1 - \epsilon)\rho_b A e^{(\frac{-E}{RT_c})} p_{\text{NH}_3} \quad [\text{mol}_{\text{NH}_3}/\text{g}_{\text{cat}}\text{h}] \quad 4.4$$

One last manipulation is to convert the NH_3 partial pressure to NH_3 concentration by assuming the ideal gas law and substituting p_{NH_3} with $C_{\text{NH}_3}RT$. The expression is further simplified by naming a new rate constant parameter k^* containing all parameters except C_{NH_3} (Equation 4.5).

$$r = C_R(1 - \epsilon)\rho_b A R T_c e^{(\frac{-E}{RT_c})} C_{\text{NH}_3} = k^* \cdot C_{\text{NH}_3} \quad [\text{mol}_{\text{NH}_3}/\text{g}_{\text{cat}}\text{h}] \quad 4.5$$

The decomposition efficiency is defined as:

$$\eta = (1 - C_{\text{NH}_3, \text{out}})/C_{\text{NH}_3, \text{in}} \quad 4.6$$

When observing η at various temperatures, Chein et al. noticed that both particle size (d_p) and porosity (ϵ) have no influence on the reaction, therefore making it temperature dominated. Knowing this, a 1D plug flow model can be applied to the reactor, allowing to observe decomposition through length as expressed where the term u corresponds to local axial velocity (Equation 4.7).

$$\frac{d(C_{\text{NH}_3}u)}{dz} = -r = -k^* \cdot C_{\text{NH}_3} \quad 4.7$$

With the ideal gas law, the ammonia concentration can be expressed in mole fraction x_{c, NH_3} (Equation 4.8a) or with η (Equation 4.8b). Then, the velocity u can be correlated with the inlet velocity u_{in} and η (Equation 4.8c).

$$C_{\text{NH}_3} = \frac{p_{\text{NH}_3}/p}{RT_c} p = x_{c, \text{NH}_3} \frac{p}{RT_c} \quad [\text{mol}/\text{m}^3] \quad 4.8a$$

$$x_{c, \text{NH}_3} = \frac{1 - \eta}{1 + \eta} \quad 4.8b$$

$$u = u_{in}(1 - \eta) = \frac{Q_{in}}{\pi R_b^2}(1 - \eta) \quad [\text{m}/\text{h}] \quad 4.8c$$

Q_{in} stands for the inlet volumetric flow rate and can be deduced from the inlet molar flow rate of ammonia F_c^{in} , the inlet density ρ_{in} and the ammonia molar mass M_{NH_3} (Equation 4.9a and 4.9b).

$$Q_{in} = \frac{F_c^{in} M_{\text{NH}_3}}{\rho_{in}} \quad [\text{m}^3/\text{h}] \quad 4.9a$$

$$\rho_{in} = \frac{p_{in} M_{\text{NH}_3}}{RT_c} \quad [\text{kg}/\text{m}^3] \quad 4.9b$$

Substituting Equations 4.8a, to 4.8c in Equation 4.7, the latter becomes a differential equation which can be integrated through `odeint` with variable substitution (Equation 4.10).

$$\frac{d(1 - \eta)}{dz} = -\frac{k}{u_{in}} \frac{1 - \eta}{1 - \eta} \quad 4.10$$

Once integrated, values of η through the reactor length are available and can be converted to mole fraction x_{c,NH_3} , x_{c,H_2} and x_{c,N_2} respectively using Equation 4.8b, 4.11a and 4.11b.

$$x_{c,H_2} = \frac{3\eta}{2(1 + \eta)} \quad 4.11a$$

$$x_{c,N_2} = \frac{\eta}{2(1 + \eta)} \quad 4.11b$$

When the mole fraction at the output of the reactor is combined with the mass conservation principle and the inlet flow rate F_c^{in} , the outlet flow rate of each component F_{c,NH_3}^{out} , F_{c,H_2}^{out} and F_{c,N_2}^{out} are established (Equations 4.12).

$$\begin{cases} x_{c,NH_3} = \frac{F_{c,NH_3}^{out}}{F_{c,NH_3}^{out} + F_{c,H_2}^{out} + F_{c,N_2}^{out}} \\ x_{c,H_2} = \frac{F_{c,H_2}^{out}}{F_{c,NH_3}^{out} + F_{c,H_2}^{out} + F_{c,N_2}^{out}} \\ M_{NH_3} F_{c,NH_3}^{out} + M_{H_2} F_{c,H_2}^{out} + M_{N_2} F_{c,N_2}^{out} = M_{NH_3} F_c^{in} \end{cases} \quad 4.12$$

Where M_{NH_3} , M_{H_2} and M_{N_2} are the molar masses [kg/mol].

Scale-up to system size

Chein et al. modeled a small-scale reactor with certain geometrical parameters and physical properties (Table 4.1).

Table 4.1: Geometric parameters and physical properties of the reactor and catalysts used in Chein et al. study [134].

Parameters	Value	Units
Reactor radius R_r	5	mm
Reactor length L_r	20	mm
Catalyst mass W	0.32	g
Catalyst mass to inlet molar flow rate ratio W/F	0-20	$\frac{g_{cat.h}}{mol_{NH_3}}$

For this study, the cracker needs to be modelled on a bigger, industrial scale. However, research on ammonia crackers for hydrogen production is scarce and still focused on bench scale prototypes. Studies on full-scale reactors and pilot plants are yet to be made [144, 145]. Therefore, the model of Chein et al. needs to be scaled up which is done in two steps. The first step to achieve this upscaling was to assume that the catalyst weight to molar rate ratio (W/F) and the catalyst density (W/V_b) are kept constant. The first ratio is also called "space time" as it characterises the residence time inside a reactor [146]. With these assumptions, both the catalyst scaled-up weight and volume can be determined using the second step.

The second step was to find industrial-scale flow rate data (F_c^{in}). Lipman et al. approximated that a production of hydrogen at a rate between $10 \text{ Nm}^3/h$ to $100 \text{ Nm}^3/h$ is required for industrial ammonia cracking to be economically attractive compared to other techniques [127]. It was thus decided to scale up the reactor to support a hydrogen production rate of $100 \text{ Nm}^3/h$. The outlet flow rates of N_2 and NH_3 were calculated (Equations 4.12) such that at least 99.5% of ammonia is cracked to prevent contamination of the fuel cell. The inlet molar flow rate of ammonia (F_c^{in}) could also be computed with the mass conservation principle of the third equation.

Next, the scaled-up catalyst weight could be obtained by combining the first assumption (i.e. constant W/F) and the scaled-up flow rate F_c^{in} . Using Chein et al. profiles of decomposition efficiency through W/F (Figure 4.3) and assuming a reaction temperature of 893.15 K, the W/F corresponding to a 99.5% efficiency was found to be $9 \text{ gcat.h/mol}_{\text{NH}_3}$. The corresponding catalyst mass is equal to 26.822 kg .

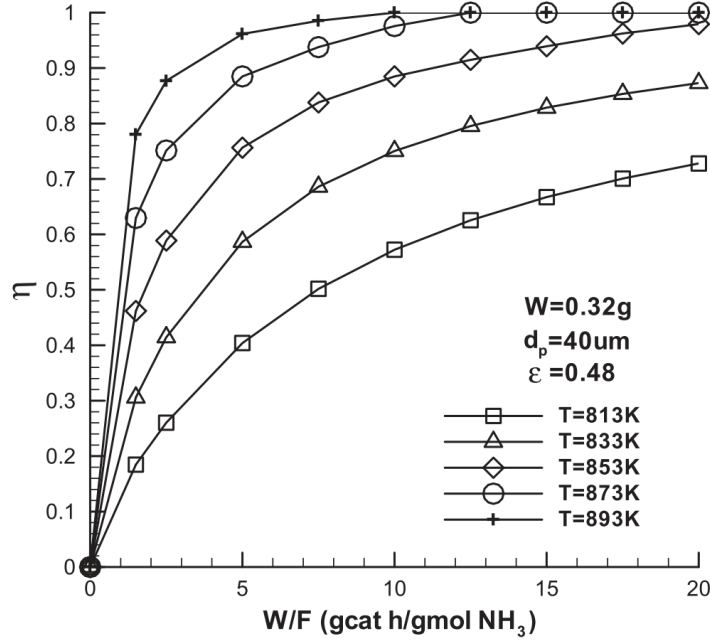


Figure 4.3: Chein et al. ammonia decomposition efficiency profiles as a function of W/F for different reaction temperatures. Extracted from [134].

Finally, using the second assumption (i.e. constant bed density) and the assumption that $V_b \approx V_r$, the scaled-up reactor volume was deduced. As the bed density ρ_b equals 203.72 kg/m^3 , the reactor volume is thus 0.132 m^3 . Considering the lack of existing full-scale cracker reactors as described before, the length L_r was fixed at a value of 1.5 m and the radius R_r was thus deduced as 0.1672 m .

In reality, the length and radius of a catalytic reactor are crucial dimensions regarding heat transfer and pressure drop. On the one hand, increasing the radius leads to a higher heat transfer coefficient, which can cause issues related to the heating of the ammonia [145, 147]. Besides, the inlet velocity also depends on the radius (Equation 4.8c). On the other hand, increasing length increases the pressure drop which is also related to the velocity and can thus lead to mass transfer limitations [145, 146]. Ultimately, a poorly dimensioned reactor could therefore have heating and pressure drop issues leading to inefficient decomposition.

Model validation

The following parameters were used to validate the model of Chein et al. [134]: a temperature T_c of 833 K ; a catalyst to ammonia flow rate ratio W/F of $10 \text{ gcat} \cdot \text{h/mol}_{\text{NH}_3}$ and a bed porosity ϵ of 0.48 . The results of this simulation are shown on Figure 4.4, where the flow composition (in molar fraction) is plotted

throughout the reactor length [mm]. The original model values are shown with dots.

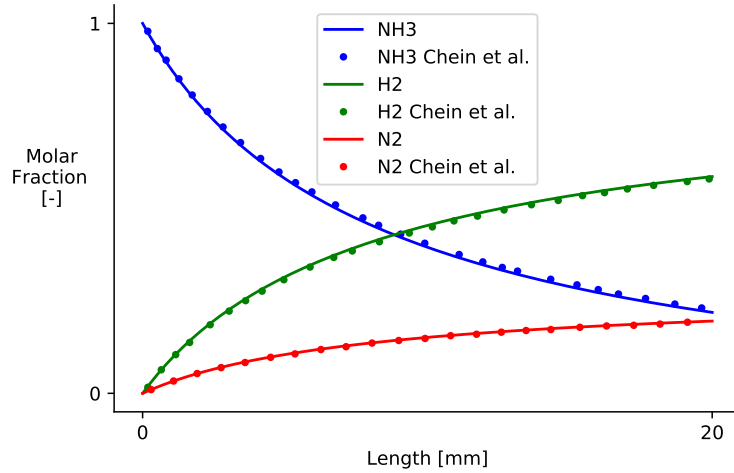


Figure 4.4: Ammonia Cracker flow composition through length. The results of Chein et al. are displayed with dots [134].

The maximum percentage of error between the results and the original model are 3.33%, 3.17% and 2.41% for the NH_3 , H_2 and N_2 molar fraction respectively.

4.1.2 Buffer tanks

The second block to be modelled are the buffer tanks. Such tanks are necessary to connect the ammonia cracker to the PEMFC stack as both operate at different flow rates. Therefore, placing buffer tanks in between allows to compensate the rate difference and assures the necessary supply to the PEMFC stack. To model this part, a straightforward *if/else* condition was implemented in Python to determine the molar content of the tanks (q_{buff}) at each second. The condition is formulated as follows for each time step t :

- *If* the amount of moles filling the tanks (q_{buff}^{in}) is larger than the amount leaving them (q_{buff}^{out}), then the tanks are filled with the difference $q_{buff}^{in} - q_{buff}^{out}$. The buffer molar content at that time step is $q_{buff}^t = q_{buff}^{t-1} + (q_{buff}^{in} - q_{buff}^{out})$.
- *Else*, the difference $q_{buff}^{out} - q_{buff}^{in}$ is emptied from the buffer. The buffer molar content at that time step is $q_{buff}^t = q_{buff}^{t-1} - (q_{buff}^{out} - q_{buff}^{in})$.

The amount of moles at the inlet (q_{buff}^{in}) and at the outlet (q_{buff}^{out}) of the buffer tanks are obtained by Equation 4.13a and 4.13b.

$$q_{buff}^{in} = F_{buff}^{in} * 1s = (F_{c,N_2}^{out} + F_{c,H_2}^{out}) * 1s \quad [mol] \quad 4.13a$$

$$q_{buff}^{out} = \frac{q_{fc,H_2}^{in}}{x_{buff,H_2}} = \frac{q_{fc,H_2}^{in}(F_{c,H_2}^{out} + F_{c,N_2}^{out})}{F_{c,H_2}^{out}} \quad [mol] \quad 4.13b$$

Where q_{fc,H_2}^{in} represents the moles consumed by the PEMFC stack for a given current; x_{buff,H_2} is the H_2 mole fraction in the buffer tanks and, by extension, in the inlet stream; and F_{buff}^{in} is the inlet molar flow rate coming from the cracker [mol/s]. As a reminder, I assumed an ideal NH_3 removal system to purify the cracker outlet stream (F_c^{out}) from any NH_3 residue entering the buffer tank. The buffer inlet stream is thus a pure mixture of H_2 and N_2 gas.

Hydrogen storage technologies exist under the form of physical, chemical and adsorption storage. In the context of large-scale H_2 storage, Wang et al. conducted a comparative study on six different physical storage systems : pipelines, pipe containers, pressure tanks, salt cavities, cryo-tanks and buffer fields. The latter technology is the one of interest for this application of short term H_2 storage. The specifications of this buffer field as given by Wang et al. are the following. The tanks are packed in bundles of 16 bottles, each bottle having a volume of 0.08 m^3 and a lifetime of 35000 cycles. The hydrogen is stored at $20 \text{ }^\circ\text{C}$ under a pressure of 300 bar . The tanks have an output pressure of 20 bar , meaning the bottles can be discharged until that pressure. The remaining gas is referred to as "cushion gas". This limitation results in a total depth of discharge of 90% [132].

To determine the volume occupied by the mixture at each time step, and therefore the filling of the bottles, both the average molar mass M_{av} [kg/mol] and specific volume v_{av} [m^3/kg] of the mixture need to be computed (Equation 4.14a and 4.14b). Specific volume data for the corresponding tanks conditions (300 bar and $20 \text{ }^\circ\text{C}$) are retrieved from Olien et al. industrial gases tables [148].

$$M_{av} = (M_{H_2}x_{buff,H_2}) + (M_{N_2}x_{buff,N_2}) \quad [kg/mol] \quad 4.14a$$

$$v_{av} = (v_{H_2}x_{buff,H_2}) + (v_{N_2}x_{buff,N_2}) \quad [m^3/kg] \quad 4.14b$$

Finally, the tanks molar content q_{buff} can be converted to the occupied volume V_{buff} (Equation 4.15).

$$V_{buff} = q_{buff} * M_{av} * v_{av} \quad [m^3] \quad 4.15$$

4.1.3 Fuel cell

The last modelled block is the fuel cell stack. The type of fuel cell chosen for the model is the Proton Exchange Membrane Fuel Cell (PEMFC).

PEMFC stack voltage model

The PEMFC was modelled according to Amphlett et al. stack voltage model [125,149,150]. The model describes the total voltage of one fuel cell as a function of the Nernst potential and three voltage losses. The total stack voltage is simply the voltage of one cell multiplied by the size of the stack (N) as the stack is arranged in serie (Equation 4.16).

$$V_{stack} = N \cdot V_{cell} = N \cdot [E_{Nernst} - V_{act} - V_{ohm} - V_{con}] \quad [V] \quad 4.16$$

The first term E_{Nernst} corresponds to the Nernst potential (Equation 4.17a). This Nernst potential is expressed by the cells temperature T_{fc} , the Gibbs free energy ΔG , the entropy ΔS and the Faraday constant F (96485 C/mol) [149]. A simplified expression is deduced, by injecting the values of the thermodynamical constants (Equation 4.17b).

$$E_{Nernst} = \frac{\Delta G}{2F} + \frac{\Delta S}{2F}(T_{fc} - 298.15) + \frac{RT_{fc}}{2F} [\ln(p_{H_2}p_{O_2}^{0.5})] \quad [V] \quad 4.17a$$

$$E_{Nernst} = 1.229 + 0.85 \cdot 10^{-3}(T_{fc} - 298.15) + 4.31 \cdot 10^{-5}T_{fc} [\ln(p_{H_2}p_{O_2}^{0.5})] \quad 4.17b$$

The ohmic overpotential V_{ohm} , the concentration overpotential V_{con} and the activation overpotential V_{act} are shown on Equation 4.18, 4.19 and 4.20 respectively.

$$V_{ohmic} = (i_{fc} + i_n) \cdot (R_M + R_C) \quad [V] \quad 4.18$$

Where R_C is the contact resistance to electron conduction [Ω]; R_M is the membrane resistance to proton conduction [Ω]; i_{fc} is the stack current [A]; and i_n is the open circuit permanent current due to fuel crossover through the electrolyte [A] [150].

$$V_{con} = -B \ln\left(1 - \frac{J + J_n}{J_{max}}\right) \quad [V] \quad 4.19$$

Where J , J_{max} and J_n are the current density, the maximum current density and the open circuit current density [A/cm^2]. They are linked to the current with A_{fc} , the active cell area [cm^2]. B is a parametric constant depending on the cell type [V].

$$V_{act} = -[\xi_1 + \xi_2 T_{fc} + \xi_3 T_{fc} \ln(c_{O_2}) + \xi_4 T_{fc} \ln(i_{fc} + i_n)] \quad [V] \quad 4.20$$

Where the four ξ_i ($i = 1...4$) factors are parametric coefficients containing thermodynamical, kinetic and electrochemical information [151]. They depend on the type of fuel cell used. Their expressions are shown in Equations 4.21a through 4.21d.

$$\xi_1 = -0.948 \quad 4.21a$$

$$\xi_2 = 0.00286 + 0.0002 \ln(A_{fc}) + (4.3 \cdot 10^{-5}) \ln(c_{H_2}) \quad 4.21b$$

$$\xi_3 = 7.6 \cdot 10^{-5} \quad 4.21c$$

$$\xi_4 = -1.93 \cdot 10^{-4} \quad 4.21d$$

Furthermore, R_M can be obtained through $R_M = \rho_M l / A$ where l corresponds to the membrane thickness [μm]. ρ_M is the membrane specific resistivity [Ωcm] (Equation 4.22).

$$\rho_M = \frac{181.6 \left[1 + 0.03 \frac{i_{fc}}{A_{fc}} + 0.062 \left(\frac{T_{fc}}{303} \right)^2 \left(\frac{i_{fc}}{A_{fc}} \right)^{2.5} \right]}{\left[\psi - 0.634 - 3 \left(\frac{i_{fc}}{A_{fc}} \right) \right] \exp \left[4.18 \left(\frac{T_{fc} - 303}{T_{fc}} \right) \right]} \quad [\Omega cm] \quad 4.22$$

Where ψ represents the membrane water content, a parametric coefficient relative to the membrane humidity and the anode feed stoichiometry [151].

Two variables remains undefined: the concentrations of the gases at the catalytic interface c_{O_2} and c_{H_2} . Both concentrations can be deduced from the partial pressures following Henry's law (Equation 4.23a and 4.23b), where H corresponds to Henry's law constants [152].

$$c_{O_2} = \frac{p_{O_2}}{H_{O_2}} = \frac{p_{O_2}}{5.08 \cdot 10^6 e^{\left(-\frac{498}{T_{fc}} \right)}} \quad [mol/cm^3] \quad 4.23a$$

$$c_{H_2} = \frac{p_{H_2}}{H_{H_2}} = \frac{p_{H_2}}{1.09 \cdot 10^6 e^{\left(\frac{77}{T_{fc}} \right)}} \quad [mol/cm^3] \quad 4.23b$$

With these equations encoded in Python, a voltage-current profile following Equation 4.16 can be computed (Figure 4.6).

Finally, the fuel cell efficiency can be computed (Equation 4.24).

$$\eta_{stack} = \mu_f \cdot \frac{V_{stack}}{N \cdot E_{HHV}^\circ} \quad 4.24$$

Where μ_F represents the fuel utilization which can be assumed constant and equal to 95% [153]. The denominator corresponds to the voltage that could be obtained if all the hydrogen chemical energy (i.e. the higher heating value $HHV_{H_2} = 285.83 kJ/mol$) was converted to electrical energy (Equation 4.25) [154].

$$E_{HHV}^\circ = \frac{HHV}{2F} = 1.481 \quad [V] \quad 4.25$$

To connect the PEMFC stack to the rest of the system, the hydrogen consumption can be approximated from the stack current (Equation 4.26) [150].

$$q_{fc, H_2}^{in} = \frac{q_{fc, H_2}^{cons}}{\mu_f} = \frac{N \cdot i_{fc}}{2F \cdot \mu_f} \quad [mol] \quad 4.26$$

The fuel utilization factor μ_f represents the ratio of consumed hydrogen q_{fc,H_2}^{cons} to the actual inlet flow rate of hydrogen q_{fc,H_2}^{in} . In reality, the fuel cell reaction is not 100% efficient and H_2 remains at the outlet. With the assumption that there is a hydrogen flow rate control at the inlet of the stack, μ_f can be assumed constant and equal to 95% [153]. Once computed, q_{fc,H_2}^{in} can be put inside Equation 4.13b to link the stack to the buffer tanks.

PEMFC transient model

Both the activation and the concentration voltage losses can be extended to a dynamical model. In fact, during current variations, the fuel cell witnesses a phenomenon called "charge double layer" at the interface between the electrodes and the electrolyte, where the charges accumulate. This accumulation causes a delay in the charge dissipation. Therefore, the cell behaves as if an electrical capacitor was placed in parallel with the two overpotential equivalence resistance $R_a = R_{act} + R_{con}$ on an equivalent electrical circuit (Figure 4.5) [150,155].

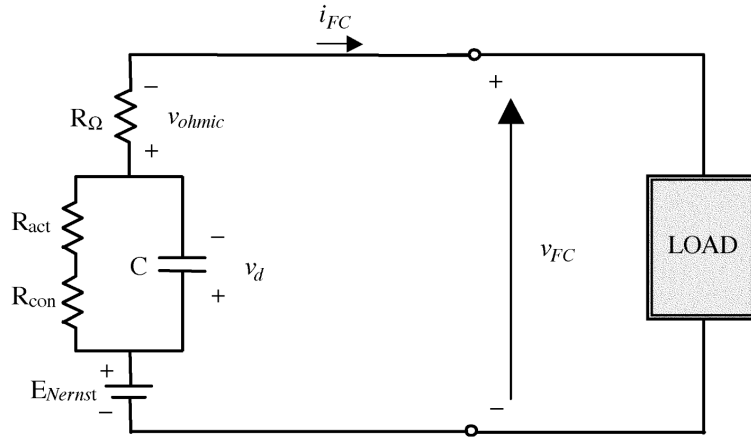


Figure 4.5: A representation of the equivalent circuit of a PEMFC. Extracted from [155].

The equivalent capacitor is characterised by a capacitance C [F] (Equation 4.27).

$$C = \frac{\epsilon A_{fc}}{d} \quad [F] \quad 4.27$$

Where ϵ is the electrical permittivity [F/m], A_{fc} is the surface area of the cell [m^2] and d is the electrodes separation [m]. In the literature, the capacitance is often given as C/A with typical values ranging between 0.013 and 0.042 F/m^2 [156]. The delay occurring in the voltage response of the cell can be expressed as a differential equation (Equation 4.28).

$$\frac{dv_d}{dt} = \frac{1}{C}i_{fc} - \frac{1}{\tau}v_d \quad 4.28$$

Where τ is an electrical time constant containing C as well as an equivalent resistance R_a (Equation 4.29).

$$\tau = C \cdot R_a = C \left(\frac{V_{act} + V_{con}}{i_{fc}} \right) \quad [s] \quad 4.29$$

The PEMFCs transient response (in [V]) can be observed by integrating the differential equation. In fact, the stack voltage from Equation 4.16 can be rewritten in Equation 4.30 to express the dynamic voltage explicitly.

$$V_{stack} = N \cdot V_{cell} = N \cdot [E_{Nernst} - V_{ohm} - v_d] \quad 4.30$$

The stack power response can also be computed as $P_{stack} = V_{stack}i_{fc}$. With these equations, both the power and voltage response can be graphically displayed (Figure 4.7 and 4.6).

Model validation

The fuel cell model was validated with the results of Correa et al. [153]. For this purpose, the real-life cell (i.e. the *Ballard Mark V* fuel cell) was simulated with the parameters given in Table 4.2.

Table 4.2: Design parameters for the Ballard Mark V fuel cell [153].

T_{fc} <i>K</i>	A <i>cm</i> ²	l <i>μm</i>	p_{H_2} <i>atm</i>	p_{O_2} <i>atm</i>	ψ —	J_{max} <i>mA/cm</i> ²	J_n <i>mA/cm</i> ²	B <i>V</i>	R_C <i>Ω</i>
343	50.6	178	1	1	23	1500	1.2	0.016	0.0003

The validation was made in two steps, where first the steady-state model was validated by observing the voltage and current profile for a unique cell (Figure 4.6). Then, the dynamical voltage and power response of a stack of 35 cells is observed for a current ramp of 50A to 150A to 50 A over a period of 10 seconds (Figure 4.7 and Figure 4.8).

The maximum error between the results and the original model for the V-I profile is 4.90%. For the dynamic response, the maximum error is 5.89% for the voltage and 7.35% for the power.

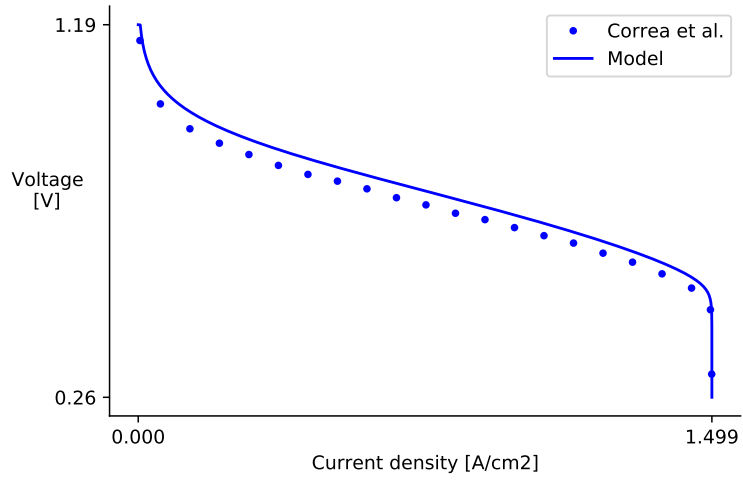


Figure 4.6: Voltage-current profile of a Ballard Mark V fuel cell. The results of Correa et al. are displayed with blue dots [153].

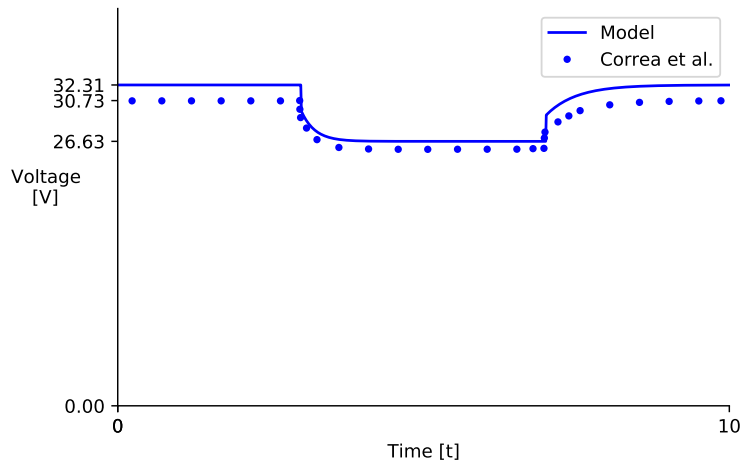


Figure 4.7: Voltage response of a 35-cell Ballard Mark V stack to a current ramp of 50A to 150A to 50 A. The results of Correa et al. are displayed with blue dots [153].

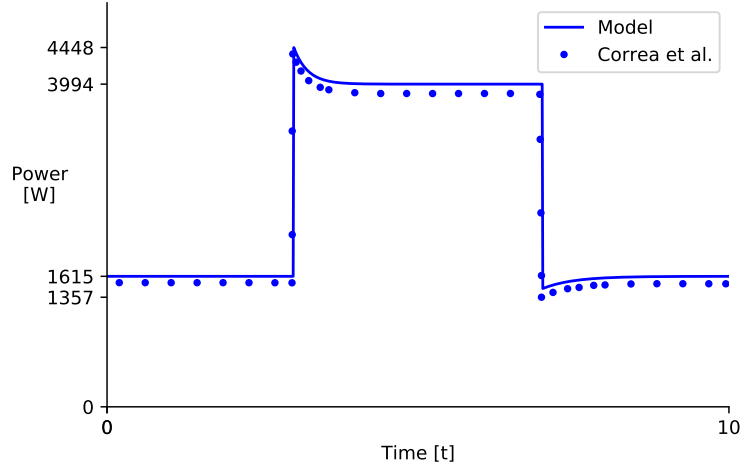


Figure 4.8: Power response of a 35-cell Ballard Mark V stack to a current ramp of 50A to 150A to 50 A. The results of Correa et al. are displayed with blue dots [153].

4.2 Multi-objective deterministic optimization

The first objectives of this research is the deterministic optimization of the system that has just been detailed. In this section, the optimization algorithm is first explained before breaking down the optimization scheme adopted for this study as well as the design specifications and boundaries.

4.2.1 Nondominated Sorting Genetic Algorithm

The optimization algorithm used in this study is the second version of the Non-dominated Sorting Genetic Algorithm (NSGA-II) developed by Deb et al. [157].

NSGA-II is a type of genetic algorithm. These algorithms - also called evolutionary algorithms - are based on an abstraction of Darwin's evolution theory by mimicking concepts such as "selection of the fittest" or "elitism", "chromosomes crossovers" and "mutations" [158]. In the context of optimization, genetic algorithms work by iteration, starting from a first generation of "parents" solutions and creating a new "offspring" generation with the aim of converging to optimized solutions along the desired objectives. The biology concepts are applied throughout the process by: sorting out the best-fit solutions to be the next parents (i.e. "selection of the fittest") and randomly varying the parents design parameters in each of their ranges to generate offsprings with a new set of parameters (i.e. "crossover" and "mutation") [159]. Besides, NSGA-II is also categorized as a multi-objective

algorithm as it can handle several optimization objectives and return multiple Pareto-optimal solutions in a single run.

Deb et al. designed NSGA-II as a new version of their previous Nondominated Sorting Genetic Algorithm (NSGA) algorithm with the aim of addressing issues such as its high computational complexity, its lack of elitism and its dependence on external user-defined parameters. To understand the algorithm's functioning, its two sorting mechanisms need to be clarified.

The first one is a nondominated sorting procedure. This procedure allows each new generation of solutions to be sorted out by determining which solutions dominate the others, and at which rank. The concept of dominance is illustrated on Figure 4.9 where a set of solutions for the minimization of two objectives (f_1 and f_2) are shown.

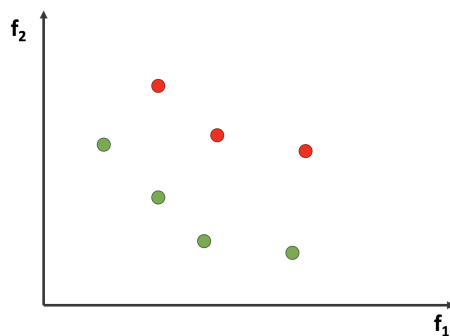


Figure 4.9: A 2D representation of solution domination between minimizing objectives f_1 and f_2 where non-dominated points (green) and dominated solutions (red) are displayed. The green points dominate the red points as each of them minimize f_1 and f_2 better.

To achieve nondominated sorting, each solution p is associated with two variables: n_p the number of solutions that dominate p , and S_p the list of solutions dominated by p . Once the generation has been sorted out, each solution is stored in a set corresponding to its domination rank: if a solution is not dominated by any other, it is stored in the list F_1 ; if it is dominated by one solution, it is stored in F_2 ; and so on...

A second procedure is used to control the solutions diversity by assessing the proximity between two solutions. The quantity of interest that is calculated during this procedure is the "crowding distance" (Figure 4.10). The crowding distance of a solution i corresponds to the perimeter of the cuboid formed by connecting the two adjacent solutions $i - 1$ and $i + 1$ with segments parallel to both objectives axis. Solutions with a smaller crowding distance are thus located in a more crowded

region. In general, when two solutions of the same domination rank are compared, the one with the largest crowding distance is preferred.

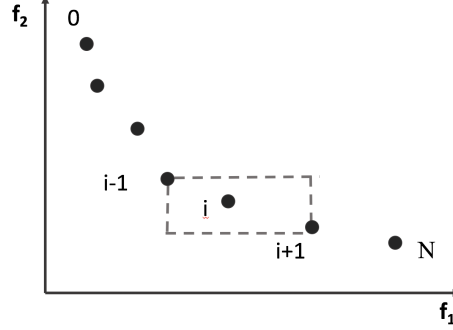


Figure 4.10: A 2D representation of crowd distance calculation in a set of solutions along 2 objectives f_1 and f_2 [157].

With these two main mechanisms, the whole optimizing loop of NSGA-II can now be summarized. For this purpose, a visual representation of the t -th generation is shown on Figure 4.11. The loop starts with the parent generation P_t containing N solutions. The first step is the creation of an offspring generation Q_t of the same size by crossover and mutation. The overall set R_t of size $2N$ containing both the parents and the offsprings is then treated with the non-dominated sorting procedure during the second step. By sorting out both the parents and their offsprings, elitism is ensured. From this first sorting, R_t has now been distributed in lists following domination ranks as explained before. The aim of this step is to find the N best solutions to become the parents generation P_{t+1} for the next iteration. The filling of P_{t+1} takes place by first taking the solutions stored in F_1 (i.e. the non-dominated ones), then F_2 , and so on until reaching F_l which is overfilling P_{t+1} . The third step makes use of the crowding distance sorting to select the solutions in the least crowded regions to finish filling P_{t+1} . At the fourth step, the new parent generation P_{t+1} is obtained and ready to perform mutation and crossover for the first step of the next iteration. It is important to note that the initial parent generation P_0 is generated randomly. In this study, Latin Hypercube Sampling was used to this end.

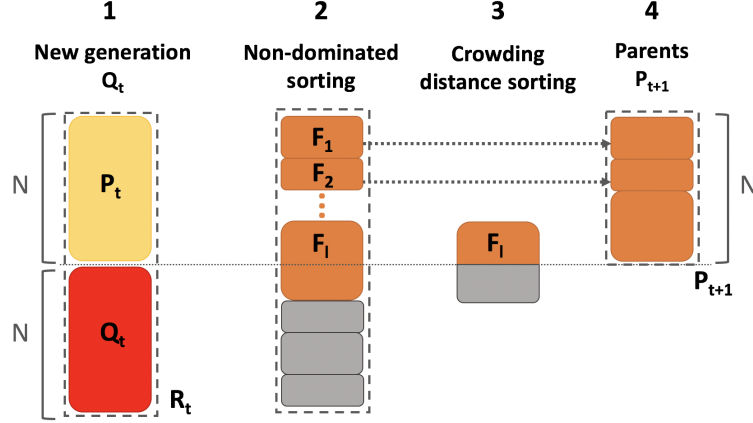


Figure 4.11: A block representation of an NSGA-II genetic optimization loop. Re-drawn from [157].

In this study, the NSGA-II algorithm was used through the *Robust design optimization of renewable Hydrogen and dErIved energy cArrier systems* framework (RHEIA) provided by Coppitters et al. [160]. The population size was set at 50 with a budget of 12500 samples, therefore generating 250 generations which was enough to reach convergence.

Beyond those direct inputs, optimization objectives, design parameters and variables also need to be detailed.

4.2.2 Demand data and objectives

Now that the algorithm has been summarized, it is crucial to break down the optimization scheme used for this research. To perform its optimization, the system is linked with real demand data of a certain location in Germany. Finally, the optimization objectives are defined.

Demand data

The objective of this study revolves around the use of an Ammonia- to-Power fuel cell installation in a stationary application where the model is optimised with real demand data. These real power demand data was retrieved via the Open Power System Data platform (OPSD) for a warehouse in Germany [161]. This warehouse is powered by photovoltaic panels. As the PV power production is not constant, the warehouse needs to complement its needs by importing electricity from the grid. The assumption is made that the ammonia-to-power system would be installed to ensure the replacement of this grid import. The data was recorded between the 28th November 2015 and the 12th October 2017. Therefore to asses a full year, data

from the year 2016 was used (i.e. 1st January 2016 until the 1st January 2017).

Optimization scheme

Four objectives have been selected and organized in a two-step optimization scheme. This separation was required to decrease the computational cost of the dynamical model. All of the objectives are assessed and optimized in one single run.

The first step of the scheme optimizes the dynamic behaviour of the PEMFC stack to make it flexible to fast changes in power demand. This dynamic behaviour has been highlighted in the model validation (Figure 4.7 and 4.8) and is characterized by applying a step change in the stack current, which leads to a capacitance-like delay in the voltage and an overshoot/undershoot in the power output. Knowing this, the two following objectives have been chosen:

- Minimization of the power overshoot/undershoot.
- Minimization of the voltage response transient time.

Minimizing both objectives could lead to an optimized design with an increased robustness to demand changes. Further connecting the stack with the required electrical converters and inverters [131] would lead to an improved voltage and current stability. allowing for a before assessing the requirements in electrical converters To assess these dynamic objectives, the warehouse demand is taken in minutes as it is the most refined data provided by the OPSD platform [161]. Then, the biggest power ramp-up and ramp-down are extracted from it to focus on the most extreme changes in current that the fuel cells could witness during the observed year. For the time period 2016-2017, the biggest ramp-up has an initial value $P_{init} = 0 \text{ W}$ and a final value $P_{final} = 1250 \text{ W}$, while the biggest ramp-down has a $P_{init} = 2390 \text{ W}$ and a $P_{final} = 406 \text{ W}$.

These power ramps can be translated to current ramps by reversing $P = V \cdot I$ and using the fuel cell V-I profile (Figure 4.6). Providing these current ramps as input to the fuel cell stack results in a dynamic voltage and power response. In the demand ramp-up case, an overshoot $\%_{over}$ is observed in the fuel cell power response and can be computed following Equation 4.31a. In the demand ramp-down case, an undershoot $\%_{under}$ is observed as in Equation 4.31b. Both quantities are characterized in percentage of the output power P_{final} to describe the fuel cell stack response [156].

$$\%_{over} = \frac{P_{over} - P_{final}}{P_{final}} \quad 4.31a$$

$$\%_{under} = \frac{P_{final} - P_{under}}{P_{final}} \quad 4.31b$$

The transient time objective is extracted from the voltage response which is defined as the time needed to reach 95% of the steady state value. The voltage response has an opposite behaviour regarding current ramps. That is, it ramps down when the current ramps up and vice versa. For a demand ramp-up, the transient time is noted τ_{over} [s] (Equation 4.32a). Conversely, the transient time is noted τ_{under} [s] for a demand ramp-down (Equation 4.32b).

$$(V_{init} - V(\tau_{over})) \geq (V_{init} - V_{final}) \cdot 95\% \quad 4.32a$$

$$(V(\tau_{under}) - V_{init}) \geq (V_{final} - V_{init}) \cdot 95\% \quad 4.32b$$

The second step of the optimization scheme includes the whole model by observing its response to a demand profile over a certain period. In particular, important questions are the capability of the PEMFC stack in reaching a power demand, and the optimization of the buffer tank sizing to ensure an adequate coupling with the ammonia cracker. To that end, the last two optimization objectives were chosen as the following:

- Minimization of the difference between the buffer tanks initial and final mass content.
- Minimization of the average difference between the power demand and the power produced by the system per time step (15 minutes).

The optimization is this time made for an observation period of 24 hours to reduce computational cost. For this purpose, the average daily power demand in 2016 was used with a time scale of a 15. minutes (Figure 4.12).

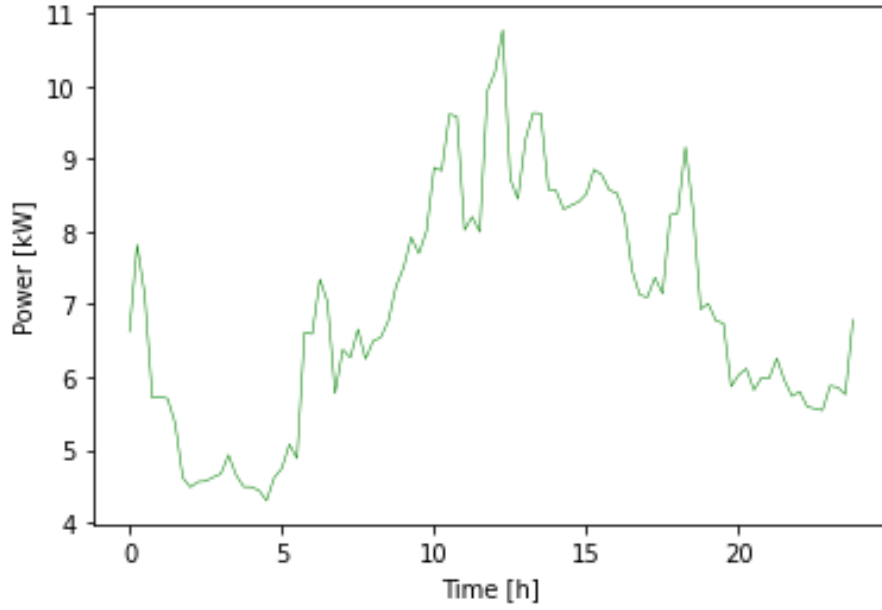


Figure 4.12: Grid power import of a German warehouse for every 15 minutes during an average day in 2016 [161]. The first 6 hours correspond to nighttime, hence the low demand. Demand then increases between 6AM and noon and decreases in the afternoon/evening.

Once this average day profile is obtained, the corresponding fuel cell stack current can be determined. To do so, the relation $P = VI$ was used, each power demand value corresponding to a specific current demand on the V-I profile of the fuel cell stack. The whole system behaviour is then assessed for each data point through a loop which computes the dynamic power response of the stack while updating the buffer content.

Once the loop is done, the system behaviour can thus be analyzed. The buffer tanks content objective Δ_{buff} is computed via Equation 4.33, where $V_{buff,i}$ is the initial tanks content and $V_{buff,f}$ is the content at the end of the day.

$$\Delta_{buff} = |V_{buff,i} - V_{buff,f}| \quad 4.33$$

The power demand and production difference objective is expressed in Equation 4.34, where i is a time index and 96 is the number of quarter hour in a day.

$$\Delta_{demand} = \frac{\sum_i |P_{demand}(t_i) - P_{stack}(t_i)|}{96} \quad 4.34$$

4.2.3 Design and boundaries

Besides the objectives, the system design needs to be specified in order to get optimized. More specifically, each design parameter of the installation need to be either fixed or chosen as a variable. The optimizer can then act on this design variable to generate different solutions. Moreover, the optimizer rejects faulty or unrealistic designs by setting boundaries on the model.

Design

There are in total 25 model parameters defined where 8 are for the ammonia cracker based on Chein et al. model [134], 2 for the buffer tanks and 15 for the PEMFC stack based on the Ballard Mark V PEMFC model [153]. Among these parameters include 9 variables and 17 fixed parameters (Table 4.3).

The design variables the reactor temperature T_c (in K), the inlet pressure p_{in} (in bar) and the ratio of the bed weight to ammonia flow rate W/F (in $gcat \cdot h/mol_{NH_3}$) to specify the ammonia cracker. The temperature and pressure bounds were retrieved from Chein et al. model [134] whereas the W/F ratio was chosen for the scale-up (Section 4.1.1). The lower limit corresponds to the lowest flow rate at which the ammonia is decomposed at 99.5% for an output of $100 Nm^3/h$ of H_2 . The upper limit corresponds to a highly reduced ammonia inlet F , therefore leading to a small production of hydrogen (Equations 4.35).

$$813 \leq T_c \leq 893 \quad 0.98 \leq p_{in} \leq 2 \quad 9 \leq W/F \leq 1000 \quad 4.35$$

Next, the number of bottles N_{bot} and their initial percents filling at the beginning of the year $\%_{fill}$ specify the buffer tanks. The upper bound for the number of bottle was determined following Wang et al. estimations for a large-scale hydrogen buffer field. The lower bound for the filling comes from the 10% depth of discharge allowed by the tanks (Equations 4.36) [132].

$$1 \leq N_{bot} \leq 7360 \quad 10 \leq \%_{fill} \leq 100 \quad 4.36$$

Finally, the number of cells in the stack N , the stack temperature T_{fc} (in K) and the membrane water content ψ specify the PEMFC stack. The temperature range comes from Dudek et al. [120] and the membrane water content values were retrieved from Correa et al. [153]. The minimum cell number was found by dividing the highest power demand of the average day (i.e. $10.77 kW$) by the highest power produced by a single cell under the poorest temperature and humidity conditions (i.e. $69 W$ at $\psi = 15$ and $T_{fc} = 328.15$). The upper bound was set to handle a $100 kW$ power demand (Equations 4.37).

$$154 \leq N \leq 1500 \quad 328.15 \leq T_{fc} \leq 353.15 \quad 15 \leq \psi \leq 24 \quad 4.37$$

Table 4.3: Parameters and values of each system part for the optimization.

Parameters	Value	Units	Source
Ammonia Cracker			
Catalyst correction factor C_r	1.5	-	[134]
Reactor temperature T_c	813 - 893	K	[134]
Reactor radius r_c	0.1672	m	[134]
Reactor length L_c	1.5	m	[134]
Bed porosity ϵ	0.37	-	[134]
Catalyst particle diameter d_p	40	μm	[134]
Reactor inlet pressure p_{in}	0.98 - 2	bar	[134]
Catalyst weight to flow rate ratio W/F	9 - 1000	$\frac{\text{gcat}\cdot\text{h}}{\text{mol}_{\text{NH}_3}}$	[134]
Buffer Tanks			
Number of bottles N_{bot}	1 - 1760	-	[132]
Initial filling $\%_{fill}$	10 - 100	%	[132]
PEMFC Stack			
Number of cells N	154 - 1500	-	
Hydrogen partial pressure p_{H_2}	1.15	bar	[153]
Oxygen partial pressure p_{O_2}	0.2095	bar	[153]
Stack temperature T_{fc}	328.15 - 353.15	K	[120]
Membrane water content ψ	15 - 24	K	[153]
Equivalent contact resistance R_C	0.0003	Ω	[153]
Cell parametric coefficient B	0.016	V	[153]
Membrane thickness l	178	μm	[153]
Cell active area A	232	cm^2	[153]
Double layer surface capacitance C/A	0.0275	F/cm^2	[156]
Maximum current density J_{max}	0.96	mA/cm^2	[153]
Open circuit current density J_n	1.2	mA/cm^2	[153]
Cell parametric coefficient ξ_1	-0.948	-	[153]
Cell parametric coefficient ξ_3	$7.6\cdot 10^{-5}$	-	[153]
Cell parametric coefficient ξ_4	$-1.93\cdot 10^{-4}$	-	[153]

Boundaries

The model was establish with boundary conditions to avoid unrealistic design in the optimized solutions. The following situations that could lead to impossible or poor designs were identified.

First, the cracker could operate under a 99.5% decomposition efficiency, leading to a too high ammonia concentration at the outlet. The assumed NH_3 -removal installation could ensure a perfect removal in such cases, but to ensure the fuel cells safety, the cracker is shut-down as soon as this situation is met, setting the outlet flow rate to zero. By doing so, the buffer tanks would eventually be emptied and the demand would thus not be met.

At the buffer tanks level, two limiting cases could be met: either each of the bottle is full but is still getting fed, or each of the bottle has reached its 10% discharge limit but is still getting emptied. In such cases, the loop browsing through the daily demand is terminated. The power production is then set to zero for the rest of the day, leading to an abnormally high Δ_{demand} objective.

Finally, one limiting case exists at the PEMFC stack level, where the power demand could be too high compared to the stack capacity. In such cases, the loop is not terminated but instead, the stack nominal power is given, leading once again to an increase in the Δ_{demand} .

4.3 Uncertainty quantification

The second objective of this research was to assess the sensitivity of the installation regarding parametric uncertainties through an Uncertainty Quantification analysis (UQ). Once again, the working principle of the algorithm is first given before detailing the integrated uncertainties on the A2P model.

4.3.1 Polynomial Chaos Expansion

The UQ algorithm is a second tool implemented by RHEIA framework and is based on Polynomial Chaos Expansion (PCE) as detailed by Sudret et al. [162].

Polynomial chaos expansion (PCE) is based on the mathematical principle that any model $\mathcal{M}$, represented by a random vector of parameters $\mathbf{X} = \{X_1, \dots, X_M\}$ and giving a random quantity of interest Y such that $Y = \mathcal{M}(\mathbf{X})$, belongs to the Hilbert space of second order random variables. This principle is valid as long as Y has a finite variance. This Hilbert space then allows the representation of Y as an infinite serie displayed in Equation 4.38, where Z_j are random variables and y_j are coefficients.

$$Y = \sum_{j=0}^{\infty} y_j Z_j \quad 4.38$$

In the polynomial chaos expansion method, the variables Z_j are chosen as orthonormal multivariate polynomials such that $Z_j = \Psi_j(\mathbf{X})$. Any of the multivariate polynomial $\Psi_j(\mathbf{X})$ can itself be built as a product of basis univariate polynomials ψ as shown in Equation 4.39. For this purpose, $\boldsymbol{\alpha} = \{\alpha_1, \dots, \alpha_M\}$ is defined as a tuple of M integers called *multi-indices* which are associated with each input X_i .

$$\Psi_{\boldsymbol{\alpha}}(\mathbf{x}) \stackrel{\text{def}}{=} \prod_{i=0}^M \psi_{\alpha_i}^{(i)}(x_i) \quad 4.39$$

Some families of basis polynomials ψ are already known and linked to standard distributions families that can characterize uncertainties. Therefore, the uniform, gaussian, gamma and beta distribution are associated respectively with the Legendre, Hermite, Laguerre and Jacobi polynomials.

Adapting Equation 4.38, a polynomial chaos expansion infinite serie representation of a model $\mathcal{M}$ looks like Equation 4.40.

$$\mathcal{M}(\mathbf{X}) = \sum_{\boldsymbol{\alpha}} y_{\boldsymbol{\alpha}} \Psi_{\boldsymbol{\alpha}}(\mathbf{X}) \quad \forall \boldsymbol{\alpha} \in \mathbb{N}^M \quad 4.40$$

To be able to transcribe it numerically, it needs to be truncated as it is still an infinite serie. This truncation can be achieved on the total degree of the polynomials $\Psi_{\boldsymbol{\alpha}}$ by selecting the polynomials characterized by a finite set of multi-indices $\boldsymbol{\alpha}$ with a size smaller than a given degree p . This finite set is called $\mathcal{A}$ and is defined in Equation 4.41a. With this truncation scheme, the infinite series becomes finite and the total number of terms it contains can be computed by Equation 4.41b. In practical application, the maximal degree p typically has a value between 3 and 5. Higher degrees can lead to a dramatic increase of the number of terms and thus of the complexity of the representation. This is mentioned in Sudret's report as the "curse of dimensionality".

$$\mathcal{A}^{M,p} = \{\boldsymbol{\alpha} \in \mathbb{N}^M : |\boldsymbol{\alpha}| \leq p\} \quad 4.41a$$

$$|\mathcal{A}^{M,p}| = \binom{M+p}{p} = \frac{(M+p)!}{M!p!} \quad 4.41b$$

Finally, the finite PCE representation of a model $\mathcal{M}(\mathbf{X})$ is shown in Equation 4.42.

$$\mathcal{M}^{PCE}(\mathbf{X}) = \sum_{\boldsymbol{\alpha}} y_{\boldsymbol{\alpha}} \Psi_{\boldsymbol{\alpha}}(\mathbf{X}) \approx \mathcal{M}(\mathbf{X}) \quad \forall \boldsymbol{\alpha} \in \mathcal{A} \quad 4.42$$

In order to complete the formula, its coefficients y_{α} now need to be quantified. This calculation is performed with a least-square minimization problem. The goal of it is to minimize the square of the residual $(\mathcal{M}(\mathbf{X}) - \mathbf{Y}^T \Psi(\mathbf{X}))^2$, where the first term of the difference is the real model and the second term is a PCE serie with a set of n sample points $\mathbf{X} \in \mathcal{X} = \{\mathbf{x}^{(i)}, i = 1, \dots, n\}$. The sample points can be generated randomly by a Monte Carlo simulation or by the Latin Hypercube Sampling method (which is the case in this research). In practice, to avoid overfitting, the rule of thumb is to take a sample size of $n \approx 2-3|\mathcal{A}|$.

The residual expressed before can be developed in a matrix form. When setting its derivative equal to zero to express the minimization, a solution expression can be computed (Equation 4.43).

$$\hat{\mathbf{y}} = (\mathbf{A}^T \mathbf{A})^{-1} \mathbf{A}^T \mathcal{Y} \quad 4.43$$

To understand this expression, two terms have to be defined. The first one, $\mathbf{A}$, is called the *information matrix* and contains the evaluation of the polynomials at each of the sample points (Equation 4.44a). The second one, $\mathcal{Y}$, is the evaluation of the model itself at each of the sample points (Equation 4.44b).

$$\mathbf{A} = \{\mathbf{A}_{ij} \stackrel{\text{def}}{=} \psi_j(\mathbf{x}^{(i)}), \quad i = 1, \dots, n, \quad j = 1, \dots, |\mathcal{A}|\} \quad 4.44a$$

$$\mathcal{Y} = \{y^{(1)} = \mathcal{M}(\mathbf{x}^{(1)}), \dots, y^{(n)} = \mathcal{M}(\mathbf{x}^{(n)})\}^T \quad 4.44b$$

At last, once the coefficients have been determined, the PCE serie approximation can be used to extract information such as its mean (Equation 4.45a) and variance (Equation 4.45b).

$$\mu = y_0 \quad 4.45a$$

$$\sigma^2 = \sum_{\alpha} y_{\alpha}^2 \quad 4.45b$$

Besides these statistical moments, the influence of each model parameter $\mathbf{X}$ on the variance of the model output Y can be analyzed to perform a global sensitivity analysis of the model. The method used in this research is the Sobol decomposition. For each parameter i , this method provides a so-called Sobol' index S_i , which is the ratio of the parameter partial variances to the total variance calculated before. Furthermore, the *total Sobol' index* S_i^T quantifies the total impact of i , including its interaction with other parameters. The total Sobol' indices formula provided by PCE is developed in Equation 4.46.

$$S_i^{T,PC} = \sum_{\alpha} y_{\alpha}^2 / \sigma^2 \quad \forall \mathcal{A}_i^T = \{\alpha \in \mathcal{A} : \alpha_i > 0\} \quad 4.46$$

A third information that can be extracted from the polynomial chaos expansion is its Probability Density Function (PDF). By generating a large enough sample set with a Monte Carlo Simulation ($n_{MCS} \approx 10^{5-6}$) and using a kernel density estimator, a continuous Probability Density Function (PDF) of Y can be plotted as shown in Equation 4.47. K designates the kernel function and h is the bandwidth:

$$f(Y) = \frac{1}{n_{MCS}h} \sum_{i=1}^{n_{MCS}} K\left(\frac{y - \mathcal{M}^{PC}(\mathbf{x}_i)}{h}\right) \quad 4.47$$

It can be useful to highlight the limitations of the PCE compared to the model, as the serie is truncated under a finite degree p . In order to estimate the accuracy of the truncation *a posteriori*, the Leave-One-Out (LOO) can be computed. This method consists in constructing several PCE by alternatively excluding each sample point $\mathbf{x}^{(i)}$. The error is then computed via Equation 4.48

$$\widehat{Err}_{LOO} = \frac{1}{n} \sum_{i=1}^n (\mathcal{M}(\mathbf{x}^{(i)}) - \mathcal{M}^{PC \setminus i}(\mathbf{x}^{(i)}))^2 \quad 4.48$$

The PCE method was also used in RHEIA. The necessary inputs are the following: the polynomial order p to which the serie will be truncated and the objective of interest (i.e. the Y output of the model $\mathcal{M}$) [160].

4.3.2 Stochastic space

The main requirement to run the UQ is the characterization of the parametric uncertainties that will act on it (Table 4.3).

Among the initial 17 fixed parameters, 15 of them have been selected as uncertain. These uncertainties can be defined in RHEIA either by Uniform or Gaussian distributions. Usually, Gaussian distributions characterize natural randomness while Uniform is preferred when there is a lack of knowledge or for operational parameters [163].

In the ammonia cracker, 3 uncertainties were considered. The reactor dimensions (i.e. length and radius) were varied within a 1% uncertainty. These dimension uncertainties were defined as Uniform as they depend on manufacturing tolerances. The uncertainty on the bed porosity was retrieved from Chein et al. range [134], where a Gaussian distribution was considered in the catalyst particle packing.

In the PEMFC stack, 11 uncertainties were considered. The uncertainty on the hydrogen partial pressure was chosen as Uniform as it depends on the pressure valve at the inlet. Its range was determined from Correa et al. lowest bound (1 bar) and Nedstack's fuel cell highest bound (1.3 bar) [85, 153]. The other Uniform

uncertainties are the membrane thickness, the cell active area and its associated capacitance as all three are related to the manufacturing [155]. The rest of the parameters (i.e. R_C , B , J_{max} , J_n , ξ_1 , ξ_3 and ξ_4) were set as Gaussian uncertainties. In fact, they either depend on the material and treatment of the electrodes and membrane or on thermodynamical and chemical properties [155]. Finally, one last uncertainty was placed on the power demand. Going back to the optimization scheme, the observation period was set as the average day of 2016. To observe the seasonal variations in the demand, the average standard deviation of the average day was computed then divided by the mean to obtain the relative deviation.

Table 4.4: Parameters, distribution (PDF), mean and deviation of each uncertain parameters in the system. The distributions are either Gaussian (G) or Uniform (U).

Parameters	PDF	Mean	Deviation	Source
Ammonia Cracker				
Reactor radius r_c	U	0.1672	$9.65 \cdot 10^{-4}$	-
Reactor length L_c	U	1.5	0.00866	-
Bed porosity ϵ	G	0.37	0.0367	[134]
PEMFC Stack				
Hydrogen partial pressure p_{H_2}	U	1.15	0.0866	[153, 164]
Equivalent contact resistance R_C	G	0.0003	$1.5 \cdot 10^{-5}$	[155]
Cell parametric coefficient B	G	0.016	$8 \cdot 10^{-4}$	[155]
Membrane thickness l	U	178	5.138	[155]
Cell active area A	U	232	6.697	[155]
Double layer surface capacitance $\frac{C}{A}$	U	0.0275	0.00837	[156]
Maximum current density J_{max}	G	0.96	0.032	[155]
Open circuit current density J_n	G	0.0012	10^{-4}	[155]
Cell parametric coefficient ξ_1	G	-0.948	0.0316	[155]
Cell parametric coefficient ξ_3	G	$7.6 \cdot 10^{-5}$	$2.533 \cdot 10^{-6}$	[155]
Cell parametric coefficient ξ_4	G	$-1.93 \cdot 10^{-4}$	$6.433 \cdot 10^{-6}$	[155]
Power demand (in kW)	G	Fig. 4.12	4.623	[155]

Chapter 5

Results and discussion

This chapter first presents the designs extracted from the 2-step 4D optimization. Then, it describes the sensitivity analysis of some optimized designs. The discussion of both the optimization and the sensitivity analysis is developed throughout the section.

5.1 Optimization

This section introduces and presents the results of the 4D optimization.

5.1.1 Step 1: Fuel cell dynamic response

The first step of the optimization was focused on the dynamic behaviour of the fuel cell stack where both the power over- and undershoot and the transient response of the fuel cell stack were minimized by determining the optimized design parameters. The stack performance was evaluated under the most extreme electrical load variation of the year 2016 by determining both the highest power ramp-up and ramp-down.

The population size was set at 50 and 276 generations were generated in total for the results to converge. The 50 solutions of the last generation are displayed on Figure 5.1. At first sight, it can be observed that the optimization has worked successfully as the set of solutions forms a Pareto-like curve. However, not all solutions appear nondominated as some peaks are present on the left hand-side of the curve, showing dominated points. These points may result from the optimization of other objectives, which could explain why they persisted at the end of the optimization.

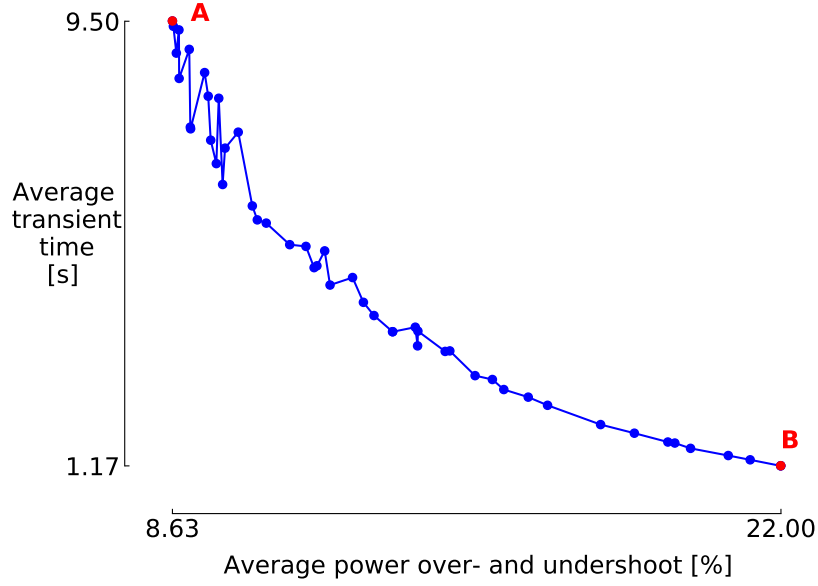


Figure 5.1: A clear Pareto front is formed by the solutions minimizing the fuel cell average power overshoot and the average transient response time. The red points A and B are the designs chosen to be compared and evaluated in the sensitivity analysis.

Several solutions from the front can be analyzed to compare their corresponding designs. For this purpose, two points have been chosen: the design minimizing the overshoots and the design minimizing the transient times. For the sake of simplicity, they will be referred to as design A and B (see highlighted point on Figure 5.1). Solution A gives a PEMFC stack with the lowest average overshoot at 8.63% (i.e. 9.53% overshoot, 8.30% undershoot). In contrast, it has the longest average response time of 9.5s (i.e. 5.3s of ramp-up, 13.7s of ramp-down). Conversely, solution B is the most rapid design with an average response of 1.17s, more than 8 times faster than solution A (i.e. 0.662s of ramp-up, 1.68s of ramp-down). However, this stack design shows the most important average overshoot at 22% which is almost 3 times higher than solution A (i.e. 29.8% overshoot, 14.1% undershoot). The dynamic power and voltage responses associated with both designs are available in the Appendix (Appendix A, Figure 6.1 through 6.8).

Table 5.1: Design parameters for the two selected solutions: minimized overshoots (A) and minimized transient times (B).

Parameters	Unit	Design A	Design B
Cracker temperature T_c	K	814	857
Cracker inlet pressure p_{in}	bar	1.022	1.007
Catalyst weight to molar flow rate ratio W/F	$\frac{g_{cat} \cdot h}{mol_{NH_3}}$	247	244
Number of cells N	-	1499	155
PEMFC stack temperature T_{fc}	K	329	353
Membrane water content ψ	-	20	16.5
Number of buffer tanks N_{bot}	-	4102	3356
Initial filling of the tanks $\%_{fill}$	%	82.5	45.1

For both these solutions, NSGA-II fixed different design variables (Table 5.1). Several design parameters can be excluded from the analysis right away. In fact, one can expect that neither the ammonia cracker or the buffer tanks influence the objectives of interest here as none of them are coupled to the PEMFC stack dynamics. This can indeed be confirmed by observing the plots of each individual parameter with regards to both objectives (Appendix D, Figure 6.14 through 6.29) which show no correlations with the objective. A coupling between the PEMFC dynamics and the other parts of the system could have been observed if a thermodynamical dimension was added to the model, taking into account the temperature regulation of the cell but also of the feed coming from the buffer tanks.

Within the remaining PEMFC parameters (i.e. the number of cell N , their temperature T_{fc} and their membrane water content ψ), the number of cells N stand out as a dominant variable over the objectives. As a matter of fact, the overshoot is reduced and the transient response increased by increasing the number of fuel cells. To further confirm this claim, the observation can be broadened to all 50 solutions by plotting N along both objectives. This shows that the average transient response time is linearly linked to N (Figure 5.2) while the overshoot is non-linearly correlated to N (Figure 5.3).

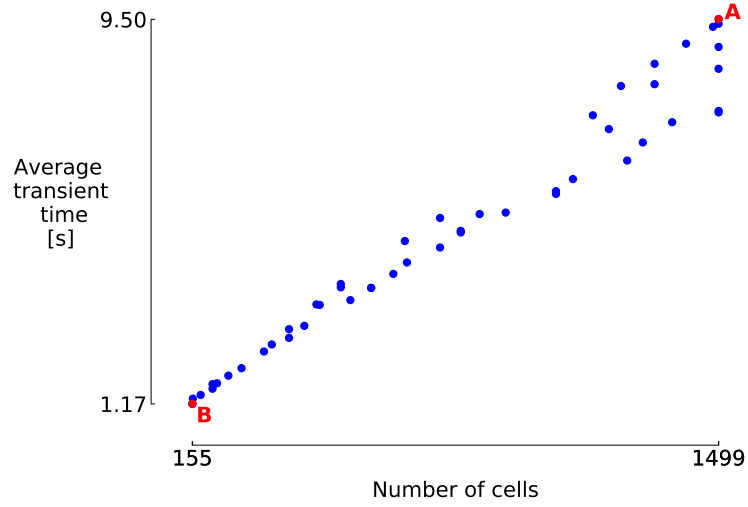


Figure 5.2: The average transient response time has a strong linear link with the number of cells in the stack. The red points A and B are the designs chosen to be compared and evaluated in the sensitivity analysis.

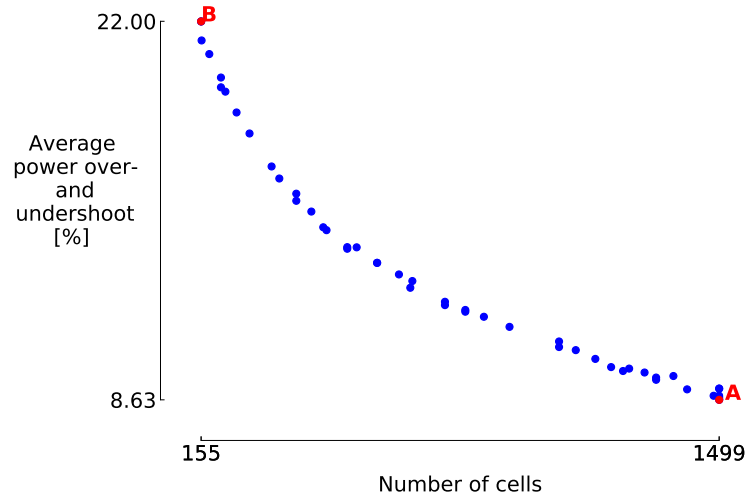


Figure 5.3: The average power overshoot appears to be non-linearly linked to the number of cells contained in the stack. The red points A and B are the designs chosen to be compared and evaluated in the sensitivity analysis.

An interpretation of these relations can be made by looking at the serie arrangement of the cells. Increasing the number of cells in the PEMFC stack for a given power demand allows to spread the latter between each of them. As the cells are stacked in serie, the stack current is the same as each individual cell current. The stack voltage

however is the sum of each individual cell voltage. Eventually, the stack power corresponds to N times the power produced by each cell ($P_{stack} = (N \cdot V_{cell}) \cdot i_{fc}$). Consequently, a bigger stack allows to divide the power demand even more over the cells. Each individual cell thus needs to generate less power. This translates in lower operating currents and larger operating voltage and efficiency (Figure 5.4 and 5.5).

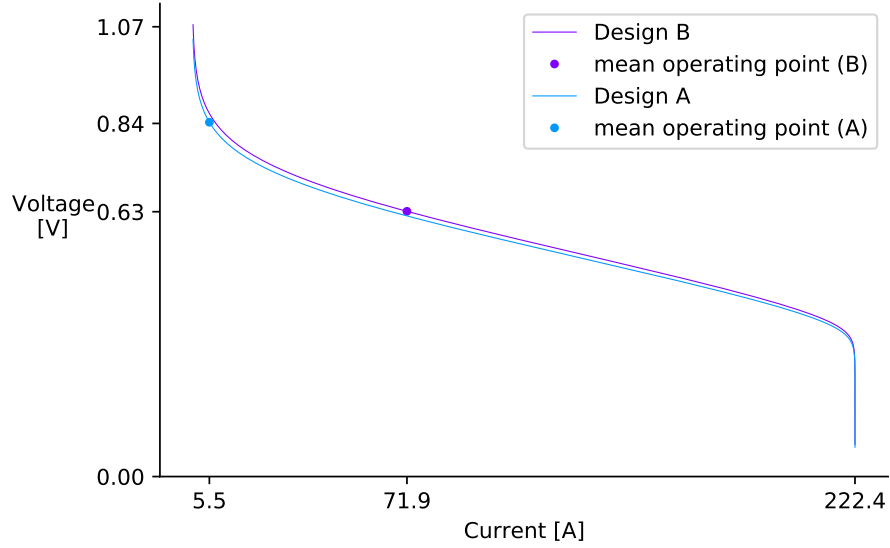


Figure 5.4: The voltage-current profile of a single cell in design A (blue) and design B (purple). The average current and voltage values are highlighted on the X and Y axis. The average operating current decreases when the cell number is increased, while the average operating voltage increases.

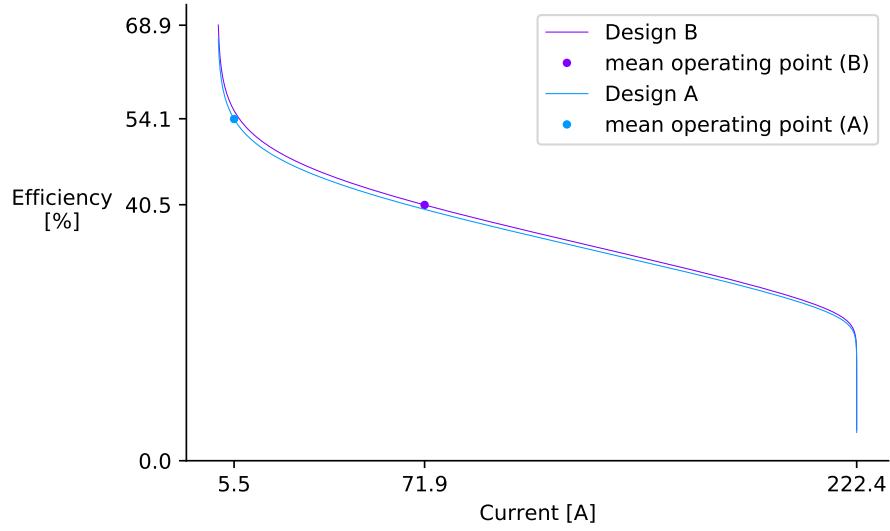


Figure 5.5: The efficiency-current profile of a single cell in design A (blue) and design B (purple). The average current and efficiency values are highlighted on the X and Y axis. The average operating current decreases when the cell number is increased, while the average efficiency increases.

Looking at the current and voltage profile during the average day for both design A (1499 cells) and B (155 cells), they indeed show different value ranges (Figure 5.6 and 5.7). The current values of design B are significantly higher with an average current of 71.9 [A], compared to design A and an average of 5.5 [A]. The average voltage of design B is lower (0.633 [V]) than design A (0.845 [V]).

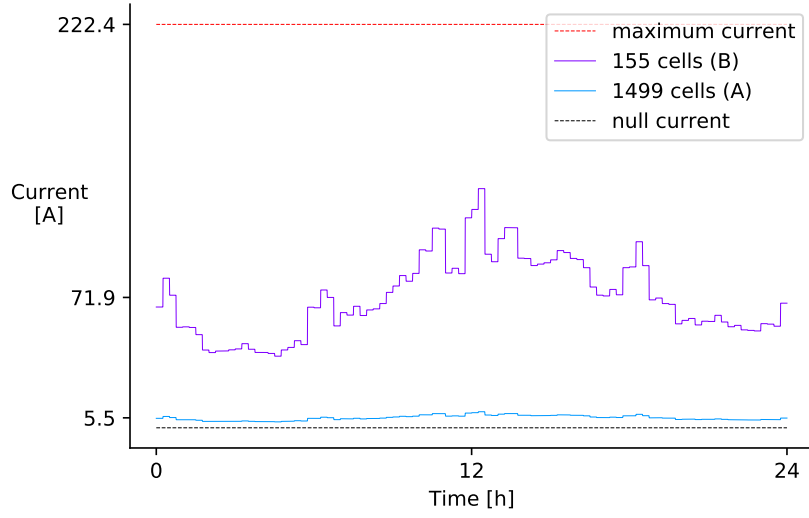


Figure 5.6: The PEMFC stack current for design A (blue) and B (purple) during an average day in 2016. The average current values are highlighted on the Y axis. The red curve highlights the cell maximum current and the black curve highlights null current. The stack current profile decreases when the cell number is increased.

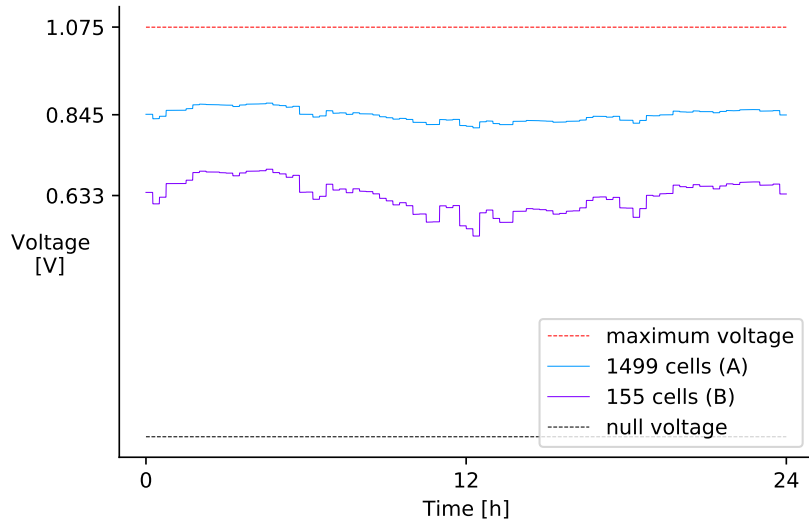


Figure 5.7: The PEMFC stack voltage for design A (blue) and B (purple) during an average day in 2016. The average voltage values are highlighted on the Y axis. The red curve highlights the cell maximum voltage and the black curve highlights null voltage. The stack voltage profile increases when the cell number is increased.

Looking back at the objectives, the link between the stack current, the over- and

undershoot and the transient response time resides in the dynamic response of the fuel cell. As explained in Section 4.1.3, the latter behaves like a capacitance characterized by the time constant τ (Equation 4.29). As the number of cell increases, the required current is reduced and each cell witnesses a smaller ramp-up and down, leading to decreased power overshoots and undershoots (respectively). Conversely, a lower current leads to an increase of the system equivalent resistance R_a and thus of τ .

In the end, a bigger stack allows for lower current ranges, which reduces the over- and undershoot but increases the transient response time constant through τ . By extension, the over- and undershoots could be neglected and the cell efficiency maximized as the number of cells tend to infinity. Such a system is unrealistic as it would be characterized by a huge resistance and currents value close to zero, leading to a slow reacting system.

5.1.2 Step 2: Daily performance

The second step of the optimization plan was to assess the whole installation performance under the average daily load of one year (2016). The two additional objectives defined for this step were the average difference between the power production and demand and the buffer mass content difference between the beginning and the end of the day.

Power production and demand gap

The optimized power production and demand gap objective shows a trade-off with the average power over- and undershoot. The lowest average over- and undershoot provides the largest power gap, and vice-versa (Figure 5.8).

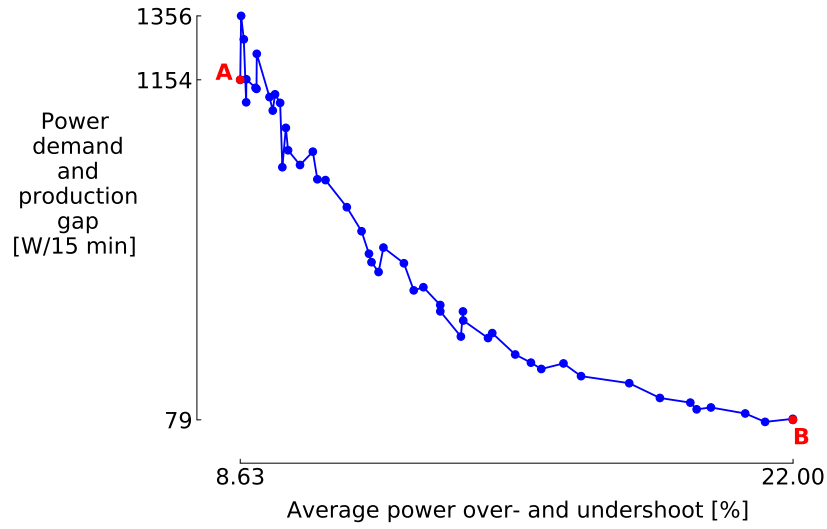


Figure 5.8: A clear Pareto front is formed by the solutions minimizing the fuel cell average power overshoot and the power demand and production gap. The red points A and B are the designs chosen to be compared and evaluated in the sensitivity analysis.

Just like the overshoot-transient curve analyzed before, this curve clearly displays a Pareto front. Additionally, the optimized power production and demand gap objective shows a linear correlation with the average transient, providing evidence that these two objectives are not competing but, on the contrary, optimized together (Figure 5.9).

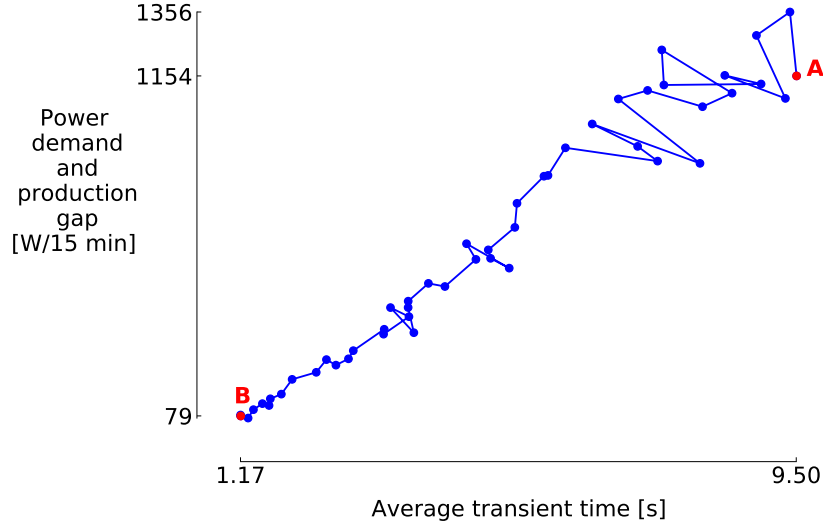


Figure 5.9: The average transient response and the power demand and production gap show a seemingly linear correlation. The red points A and B are the designs chosen to be compared and evaluated in the sensitivity analysis.

When assessing the design detailed in the previous step (A and B), they show the same pattern as for the transient response: design A minimizes the overshoot at the expense of the power gap ; and design B minimizes the power gap at the expense of the overshoot. Looking closer at the curves, design A and B actually do not correspond to the maximum and minimum power gap (respectively). Design A lead to a power gap of 1154 [W/15 min] compared to an actual maximum of 1354 [W/15 min], while design B lead to a power gap of 79 [W/15 min] compared to an actual minimum of 72 [W/15 min]. In fact, some parameters that play a role in the optimization of the overshoot and the transient may influence the power gap value slightly differently. As the power demand and production gap is linear with the transient response, and for the sake of consistency and continuity in the analysis, design A and B were kept for this objective too.

The reason behind the relationship between the three objectives can be extended from what has been discussed before. As the number of cells increases and the overshoots get minimized, the fuel cells take longer to reach steady state and the overall gap increases. Conversely, when the number of cells is minimized, the system reacts faster and the overall gap in power is decreased (Figure 5.10). In the first case, even though the overshoots are minimized, the power gap is still the biggest and vice-versa with the second case. The reason resides in the transient response time which dominates the overshoot when considering power production and demand gap. The explanation behind this could be that the overshoots take

place instantly at each current switches but for a brief amount of time, whereas the transients cause a gap spread in time (Appendix A, Figure 6.1 through 6.8). The transient time is therefore critical to this power gap objective.

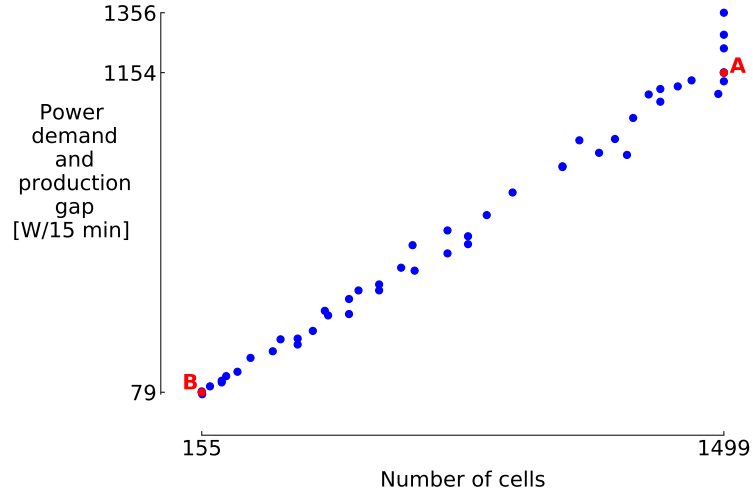


Figure 5.10: Like the average transient response, the power demand and production gap has a strong linear link with the number of cells in the stack. The red points A and B are the designs chosen to be compared and evaluated in the sensitivity analysis.

Nonetheless, the power gap values ($79\text{--}1154\text{ W/15min}$) still appear important considering the power demand is in the range of $4000\text{--}11000\text{ W}$ (Figure 4.12). The highest gap corresponds to almost 10% of the highest average demand. Actually, it is important to recall that this objective has been defined as the absolute difference, including both positive and negative gaps. These gaps appear differently when they are decomposed in power deficit (i.e. positive difference) and excess of power (i.e. negative difference), as shown in Table 5.2.

Table 5.2: Decomposition of the power production and demand gap for the three designs A and B.

Solutions	Power deficit (W/15min)	Excess power (W/15min)
A	5.57	1149
B	3.3	75.9

The power deficit values (5.57 W/15min and 3.3 W/15min for design A and B) are low compared to the excesses of power (1149 W/15min and 75.9 W/15min for

design A and B). The variation between each design is also different: the power deficit of solution A is 1.7 times more important than solution B, while the excess is 15.1 times bigger. A first explanation behind this scale difference may stem from the difference between the overshoot and the undershoot. In fact, the undershoot (Figure 6.3 and 6.4) are seemingly less important than the overshoots (Figure 6.1 and 6.2). A second explanation could reside in the working principle of the model code. In fact, slight inaccuracies could come from the discretization of the fuel cell V-I characteristic curve, which dictates the power output values. As the power gap objective is defined as a sum, these inaccuracies are accumulated which may lead to higher gap values than what a real installation would witness.

Other than the influence of the number of cells, no design variables seem to influence on the power production and demand gap, as can be seen when displaying each variable along the objective (Appendix D, Figure 6.38 to 6.45).

In the end, it appears clearly that the over- and undershoot objective competes with both the transient response time and the power demand-production gap objectives. Considering recent literature, technologies to control over- and undershoots via control systems such as Model Predictive Control and PI controller [131,165] are starting to get developed. Therefore, focusing on minimizing the transient response and the power demand-production gap is crucial to the objective of developing a flexible system.

Buffer mass content gap

The fourth objective focused on minimizing the buffer content difference at the end of the day with the intent to optimize the PEMFC stack and ammonia cracker junction. Unfortunately, the algorithm could not reach any optimized design for this parameter (Appendix C, Figure 6.11 through 6.13; Appendix D Figure 6.30 through 6.37). As the buffer tanks model solely depends on the inlet and outlet flow rates, its failure to be optimized may be due to the lack of flexibility of the ammonia cracker. In fact, the latter operates at a constant ammonia flow rate which is fixed for one design. As in reality, the power demand varies throughout the day - and by extension throughout the year - so does the fuel consumption. Instead of keeping the same flow rate as if the cracker was working non stop, one strategy of improvement could be to implement a variable flow rate, which could be useful when the buffer is in excess or in shortage of fuel. The particular difficulty to achieve this is the lack of data regarding the dynamic behaviour of an ammonia cracker, where this study used a steady state model. By implementing these modifications, the outcomes of the NSGA-II regarding the buffer content could change and lead to an optimization of the buffer sizing.

5.2 Uncertainty quantification

Once the system was optimized through NSGA-II, an uncertainty quantification was performed on different system designs. In what follows, the sensitivity of each objective with regards to parametric uncertainties is presented through probability density functions and Sobol' indices.

5.2.1 Objective 1: average overshoot

The designs chosen to be analyzed are the same that were assessed in the optimization results. They represent namely a minimized fuel cell power overshoot (design A) and a minimized transient response time and power demand-production gap (design B). In total, 15 uncertainties were assessed (Table 4.4). For the Polynomial Chaos Expansion, the polynomial order was set at 2 and 100000 samples were generated randomly to draw the Probability Density Functions (PDFs).

Distribution and PCE error

First, the PDFs of each design around their average overshoot value can be analyzed (Figure 5.11). For each design, the statistical moments describing the PDFs are detailed in Table 5.3.

A first result to look at is the Leave-One-Out (LOO), which gives an indication on the accuracy of the PCE representation of the actual model. A general rule of thumb is to keep a LOO error lower than 1%. Higher than that, it is advised to change the polynomial order [160]. This is the case for solution A which shows a LOO error of 5.37%. Unfortunately, changing the polynomial order to 1 or 3 only but increases the LOO error. This has to be kept in mind as it will directly influence the Sobol' indices, therefore showing a behaviour further from the actual model.

Table 5.3: PCE representation specifications for the average overshoot objective with regards to design A and design B: mean, standard deviation and Leave-One-Out (LOO) error.

Solutions	Mean (%)	Standard deviation	LOO error (%)
A	8.84	0.664	5.37
B	22.07	1.59	0.0129

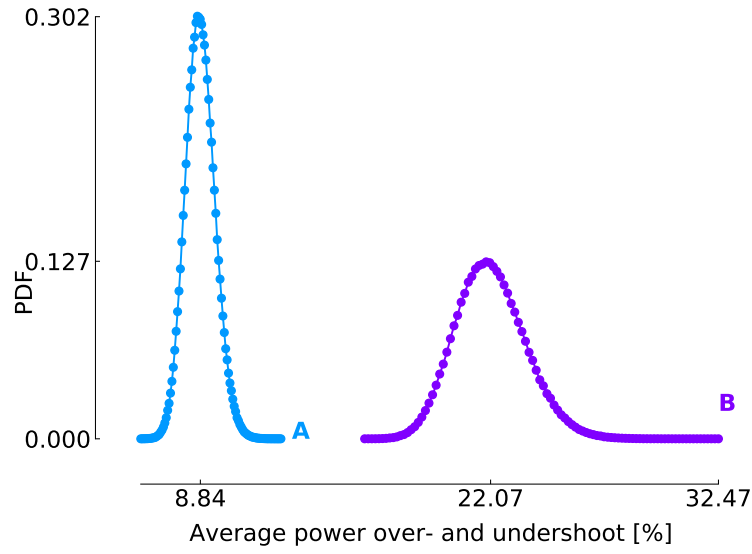


Figure 5.11: PDF of the overshoot of design A (blue) and B (purple).

Both PDFs appears to follow a Gaussian distribution. Generally speaking, the more the design shows a high average overshoot, the higher the standard deviation appears.

Sobol' indices

Next, the Sobol' indices of the average over- and undershoot objective can be assessed (Figure 5.12).

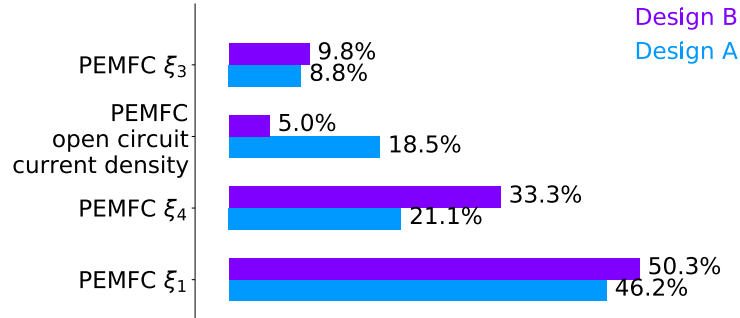


Figure 5.12: Sobol' indices for the average over- and undershoot objective with respect to design A and design B.

As can be seen, the main sensitive parameters for both designs are the PEMFC parametric coefficients ξ_1 (46.2% and 50.3% for design A and B) and ξ_4 (21.1% and 33.3% for design A and B). Some variations occurs in the less sensitive parameters.

In fact, design A appears to be more sensitive to the open-current density of the PEMFC J_n (18.5%), whereas design B is almost four times more robust to it (5%). Finally, a third PEMFC parametric coefficient ξ_3 shows a relatively similar influence on both designs (8.8% and 9.8% for design A and B). The 11 remaining uncertainties have a negligible influence.

An interpretation of these results resides in the use of the parametric coefficient ξ_1 , ξ_3 and ξ_4 . These coefficients define the activation overpotential V_{act} , where they are critical for the V-I profile of the fuel cell. Overall, their high sensitivities seem to coincide well with the literature. Indeed, the parametric coefficient ξ_1 has shown the highest degree of sensitivity in multiple studies [155, 166–168]. In some papers however, the influence of ξ_3 and ξ_4 is depicted differently, with ξ_3 appearing more sensitive than ξ_4 , contrarily to what is observed in the UQ analysis of designs A and B [155], while a more recent study observed the same order of sensitivity observed here [166]. The reason behind these dominance comes from the definition of the parametric coefficient. As they are defined by the electrochemical and thermodynamical properties of the electrodes, they are difficult to measure with great accuracy.

A second, less sensitive parameter, is the open circuit current density (J_n), which appeared to be more critical for design A than for B. This observation seems rather logical considering J_n determines the values of low currents. Therefore, as design B has the smallest fuel cell stack and thus the highest currents (Figure 5.6), it is less impacted by J_n than design A.

5.2.2 Objective 2: average transient time

Distribution and PCE error

The sensitivity analysis of the second objective (i.e. average transient response time) is first highlighted with the PDF of design A and design B around their average response times (Figure 5.13).

The Leave-One-Out validation highlights a good accuracy of the PCE representations in this case, with errors of 0.0276% for design A and 0.0149% for design B (Table 5.4).

Table 5.4: PCE representation specifications for the average transient response time with regards to design A and design B: mean, standard deviation and Leave-One-Out (LOO) error.

Solutions	Mean (s)	Standard deviation	LOO error (%)
A	9.44	3.17	0.0276
B	1.17	0.373	0.0149

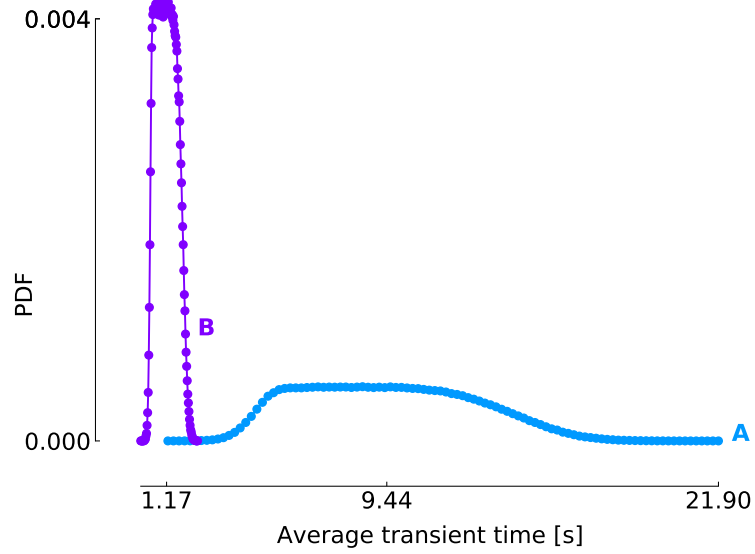


Figure 5.13: PDF of the average transient time of design A (blue) and design B (purple).

Both PDFs draw a kind of mixed distribution between Gaussian and Uniform. The Uniform disposition seems to be the expression of the surface capacitance C/A parametric uncertainty, which is itself defined with a Uniform distribution.

Sobol' indices

The Sobol' indices highlight the influence of three parameters (Figure 5.14).

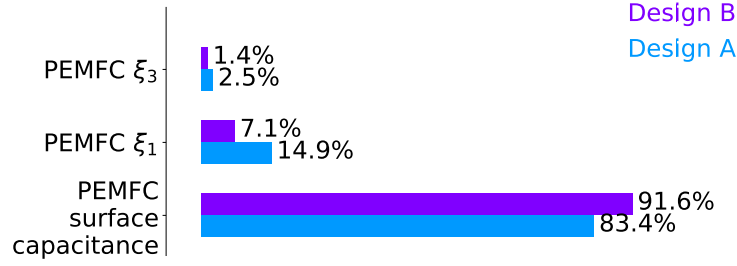


Figure 5.14: Sobol' indices for the average transient time of design A and design B.

In both designs, it appears clearly that the equivalence surface capacitance C/A [F/cm^2] is the dominant parameter regarding uncertainties. The Sobol' index equals 83.4% and 91.6% for designs A and B respectively. As C/A is characterized by a Uniform distribution, its dominance can be observed directly in the PDF, which almost draw Uniform distributions (less visible for design B).

This dominance of the surface capacitance uncertainty on the fuel cell average transient response time can be explained by the definition of the transient response itself, which is directly linked to its equivalent time constant τ . This time constant showed that the overshoots and transient response are the competing objectives. Apart from the cell current, τ is also linearly related to the equivalent capacitance of the cell: C . This relation explains the highly-sensitive nature of the average transient of the PEMFC stack with respect to C/A . As exposed by Larminie et al. the capacitance depends on the active surface area of the electrodes and the spacing between them [150]. Any factors influencing the spacing (such as thermal expansion or vibrations) but also the surface of the electrodes (degradation, oxidation) are the sources of uncertainties. Paying special attention to the stability of the stack regarding these factors could help limiting this dominant uncertainty.

A few less impacting parameters stand out such as ξ_1 and ξ_3 , which are still negligible compared to the importance of the surface capacitance. The explanation behind their slight influence on the transient response is the same as for the average overshoot objective.

5.2.3 Objective 3: buffer mass content gap

Considering that no optimized designs were reached for the buffer content objective, its uncertainties were not evaluated.

5.2.4 Objective 4: power demand and production gap

Distribution and PCE error

The final objective to quantify is the power demand and production gap. It must be noted that unexpected results arised regarding the PDF. More precisely, the uncertainty quantification for design A and B both showed what appears to be a straight line (Figure 5.15). When looking at the corresponding statistical moments (Table 5.5), it can be seen that the standard variation of design A and B are almost 4 and 2 times greater then their respective means. The means themselves are far greater than the actual value of the gap (i.e. 1154 and 79 $W/15min$ respectively). Regarding the LOO errors, they also show enormous values (91.07% and 20.3% for design A and B) which is a sign that the results are unusable. Unfortunately, these results couldn't be improved, even by changing the polynomial order to 1 or 3. Greater orders lead to unworkable computing cost.

The reasons behind these erratic results may be an indicator of a high sensitivity of the designs to a certain parameter. Another reason is the functioning of the model itself when encountering a limiting case. More specifically, when the buffer tanks are emptied beyond their depth of discharge, the whole system is shut down and the power production is set to zero for the rest of the day, leading to an enormous gap value.

Table 5.5: PCE representation specifications for the power demand and production gap with regards to design A and design B: mean, standard deviation and Leave-One-Out (LOO) error.

Solutions	Mean ($W/15min$)	Standard deviation	LOO error (%)
A	190870	705349	91.07
B	524075	1184226	20.3

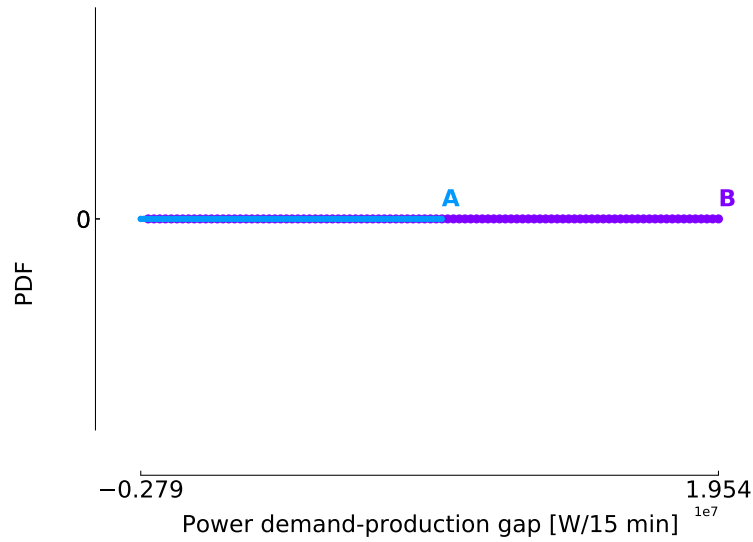


Figure 5.15: PDF of the power demand and production gap of design A (blue) and design B (purple).

Sobol' indices

In spite of the unusable results, the Sobol' indices could still be observed to search for further explanation on the source of the failure (Figure 5.16).

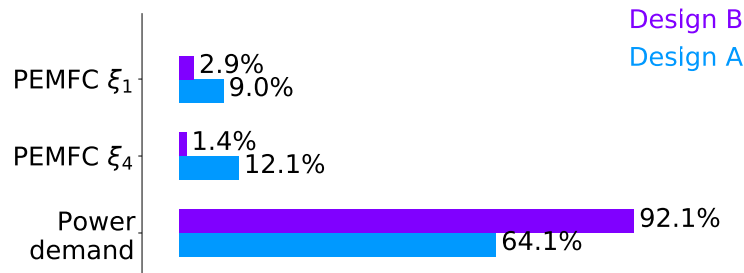


Figure 5.16: Sobol' indices for the power demand and production gap of design A and design B.

Something immediately appears in the Sobol' indices: the power demand variation has a high influence. Design B is obviously dominated by it with a 92.1% Sobol' index. Design A seems slightly less dominated (64.1%). In the latter case, other parameters such as ξ_4 and ξ_1 can be observed as having a light influence on the sensitivity (12.1% and 9% respectively). As both parameters are sources of uncertainties for the cells overshoots and transients, it seems quite logical that they are also represented on the larger scale of the whole system. This explanation is all

the more important given the correlation between the power gap and the two cells objectives, as discussed in the optimization results.

The importance of the power demand variation is here highlighted and is most certainly one of the reason behind the failure of the model during this sensitivity analysis. The modelling limitations and imperfections appear more clearly, with the implementation of the buffer tanks and their boundaries being the loophole of the model.

Chapter 6

Conclusion

As the global deadline of fossil fuel depletion approaches and climate change issues grow in importance, finding sustainable alternatives for the future of power production is undoubtedly critical. Among several options to achieve this change are the hydrogen fuel cells. Such a technology is both clean of any exhaust and flexible in its stackable nature, showing a promising future. However, although this solution appears ideal, issues arise at its very source as hydrogen is not the easiest component to produce and above all, store. To tackle this major obstacle, ammonia as an energy carrier appeared as a solution for several researchers in a so-called Ammonia-to-Power pathway.

After highlighting the existing research on the Ammonia-to-power pathway, comparing fuel cells to combined cycle gas turbines, this thesis has proposed a model for simulating a stationary installation providing power to a warehouse in Germany. The model consists of an ammonia cracker, a buffer field and a Proton Exchange Membrane Fuel Cell (PEMFC) stack. A first complication emerged during the modelling of the ammonia cracker, highlighting the lack of advancements in industrial-scale reactors.

Once the model was complete, a multi-objective deterministic optimization was performed through an implementation of a Nondominated Sorting Genetic Algorithm (NSGA-II). It allowed to minimize four objectives, formulated in a two-step scheme.

The first step revolved around the optimization of the dynamic PEMFC stack behaviour to demand variations. There, a trade-off between short stack responses and low power over- and undershoots was emphasised. The series-stacked cell size was brought to light as a critical design parameter to consider from this observation. A too small stack leads to inevitably high power over-and-undershoots. Conversely, a too large stack increases the system internal resistance and therefore the response

time, leading to a less flexible system regarding power demand fluctuations.

In a second step, the overall system was assessed regarding its performance and sizing. The importance of an optimized fuel cell response time was further confirmed by observing the gaps between the power production and demand. Unfortunately, an inconsistency was brought to light regarding the sizing of the buffer tanks, which failed to reach an optimized result. This failure highlighted the limitations of the ammonia cracker model, which only considers fixed and constant flow rate, therefore conflicting with designing a flexible power plant.

Overall, two optimized design were highlighted. On the one hand, minimizing the transient response time lead to a 155-cells stack with an average power over- and undershoot of 22%, an average transient time of 1.17 seconds and a power production and demand gap of 72 *W* each 15 minutes. On the other hand, minimizing the over- and undershoots lead to a 1499-cells stack with an average over- and undershoot of 8.63%, an average transient time of 9.5 seconds and a power production and demand gap of 1154 *W* each 15 minutes.

Finally, the system sensitivity was evaluated through Polynomial Chaos Expansion (PCE). The same two optimized designs were assessed. Firstly, it was found that the fuel cells were sensitive to the uncertainty of the thermodynamical electrochemical parameters influencing their activation overpotential (covering between 76,1% and 93,4% of the overall uncertainty). The inaccuracy arising from their measurements and modelling has significant influence on the power requirements. Moreover, the dynamic performance was observed highly sensitive to the fuel cell equivalent capacitance (between 83,4% and 91.6%), a critical and determining parameter for the stack dynamic response. As this uncertainty depends on the electrodes and their spacing, assessing their life cycle and stability could allow to reduce uncertainties. Lastly, when assessing the power demand and production gap, the obtained PCE model was extremely inaccurate and generated inconsistent values. Nevertheless, interpretations of this second failure lead to the conclusion that extremely high uncertainties arise from the power demand variation throughout the year (between 64,1% and 92,1%).

In conclusion, precisely optimizing the fuel cells properties on the one hand, and their stacking on the other hand, is necessary to ensure a flexible system able to answer rapidly to a demand. Further studies focusing on the ammonia cracker dynamic behaviour and taking into account electrical controllers for the fuel cell stack performance are required to allow a more complete and realistic optimization of the system presented in this thesis. Additionally, the uncertainty quantification can be included in the optimization process to perform a robust optimization, which takes the parametric uncertainties into account in the optimized designs.

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Appendix

A Dynamic response of optimized designs

A.1 Power overshoot

Design A: minimized over- and undershoots

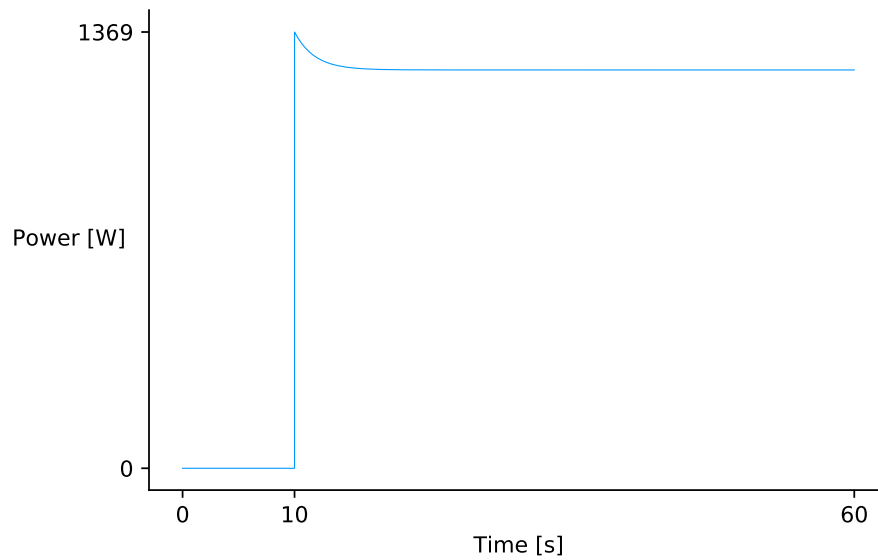


Figure 6.1: Power response of a 1499-cells PEMFC stack to the biggest demand ramp-up (0 W to 1250 W).

Design B: minimized transients

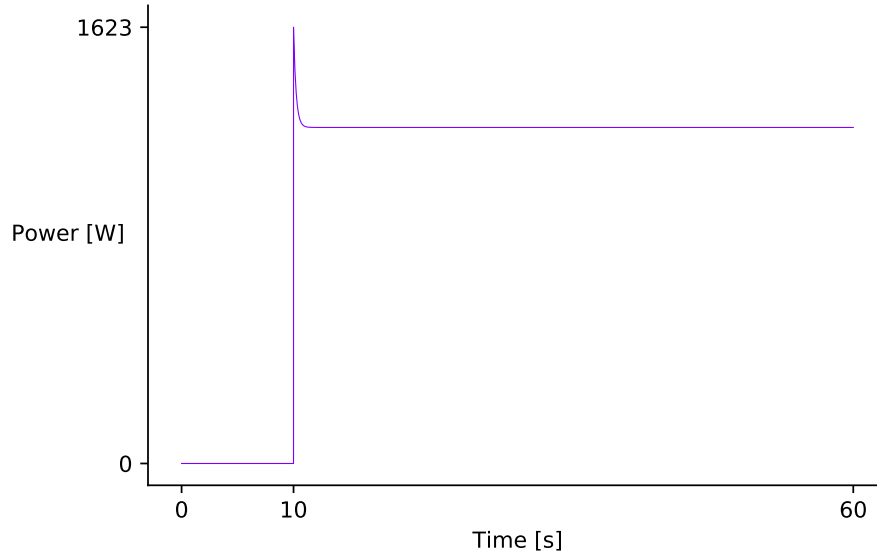


Figure 6.2: Power response of a 155-cells PEMFC stack to the biggest demand ramp-up (0 W to 1250 W).

A.2 Power undershoot

Design A: minimized over- and undershoots

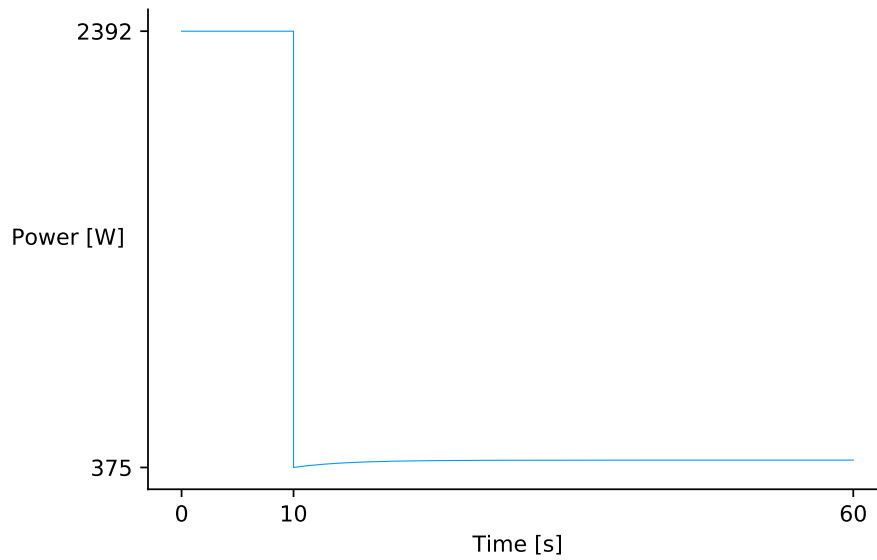


Figure 6.3: Power response of a 1499-cells PEMFC stack to the biggest demand ramp-down (2390 W to 406 W).

Design B: minimized transients

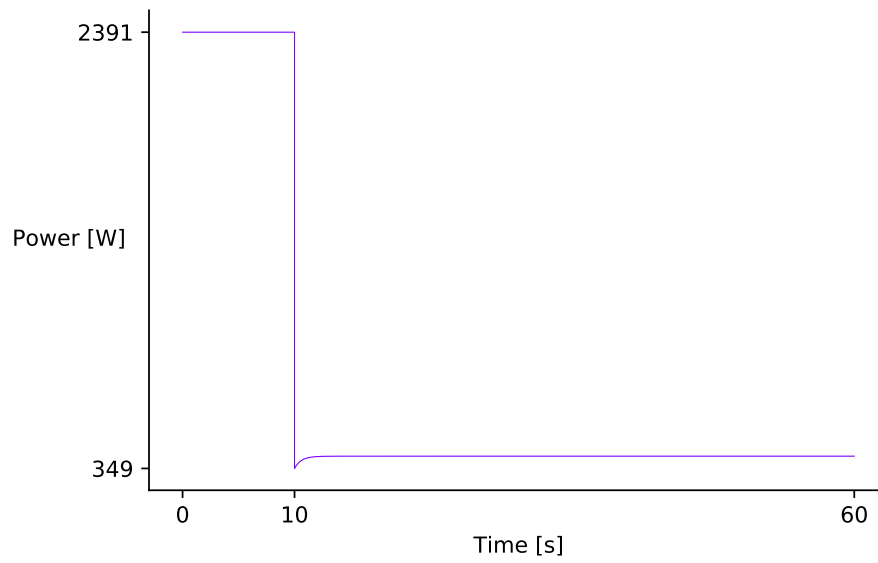


Figure 6.4: Power response of a 155-cells PEMFC stack to the biggest demand ramp-down (2390 W to 406 W).

A.3 Voltage overshoot

Design A: minimized over- and undershoots

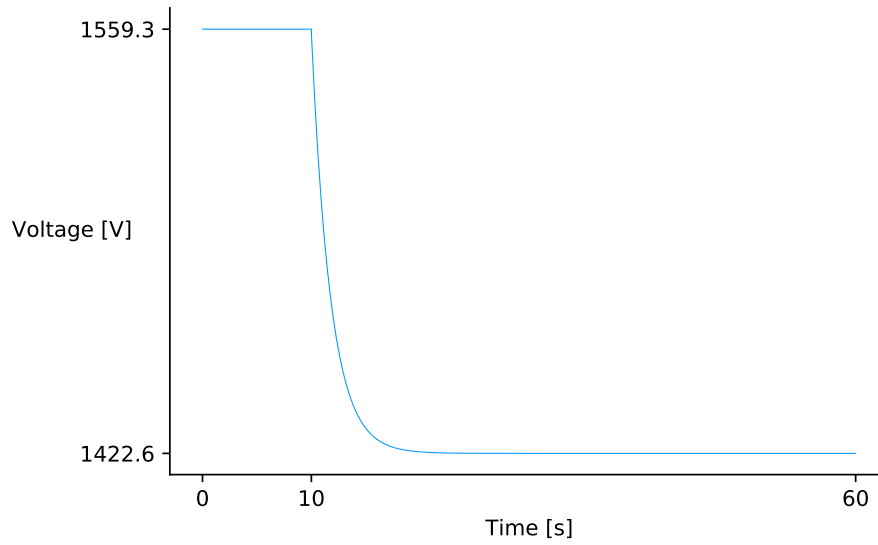


Figure 6.5: Voltage response of a 1499-cells PEMFC stack to the biggest demand ramp-up (0 W to 1250 W).

Design B: minimized transients

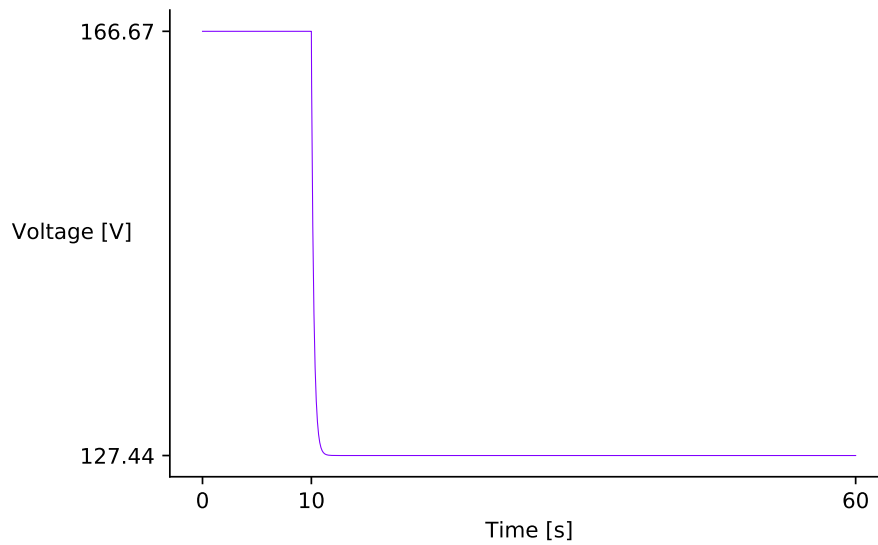


Figure 6.6: Voltage response of a 155-cells PEMFC stack to the biggest demand ramp-up (0 W to 1250 W).

A.4 Voltage undershoot

Design A: minimized over- and undershoots

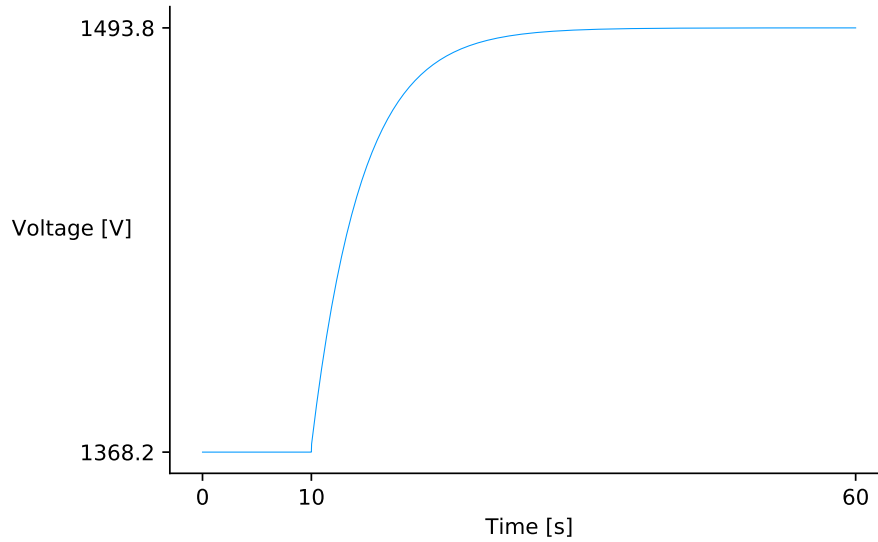


Figure 6.7: Voltage response of a 1499-cells PEMFC stack to the biggest demand ramp-down (2390 W to 406 W).

Design B: minimized transients

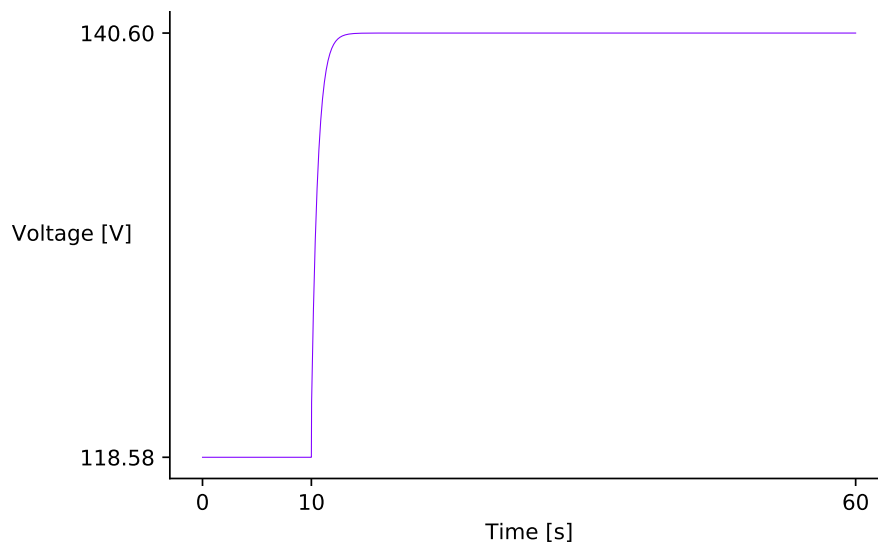


Figure 6.8: Voltage response of a 155-cells PEMFC stack to the biggest demand ramp-down (2390 W to 406 W).

B Power demand and production curves

B.1 Design A: minimized average over- and undershoot

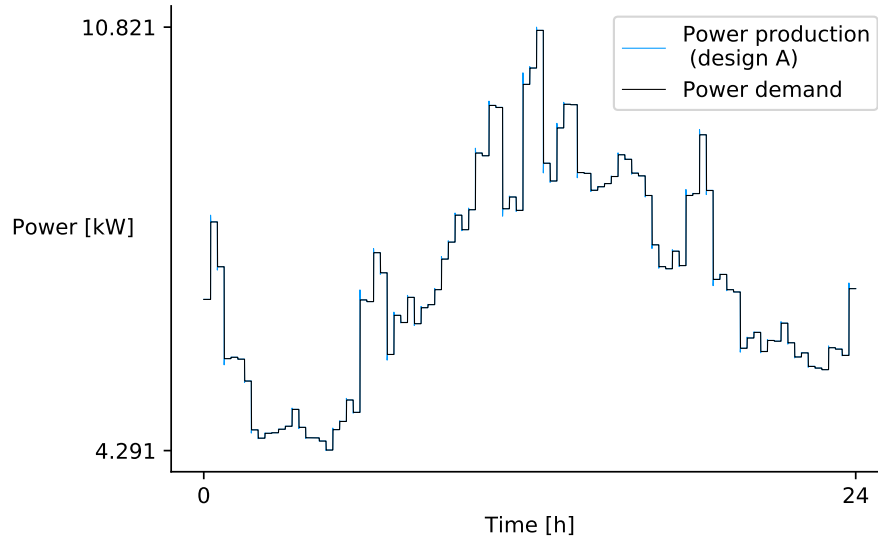


Figure 6.9: The power demand (black) and production (blue) for the average day of 2016 with the minimized average over- and undershoot design.

B.2 Design B: minimized average transient response

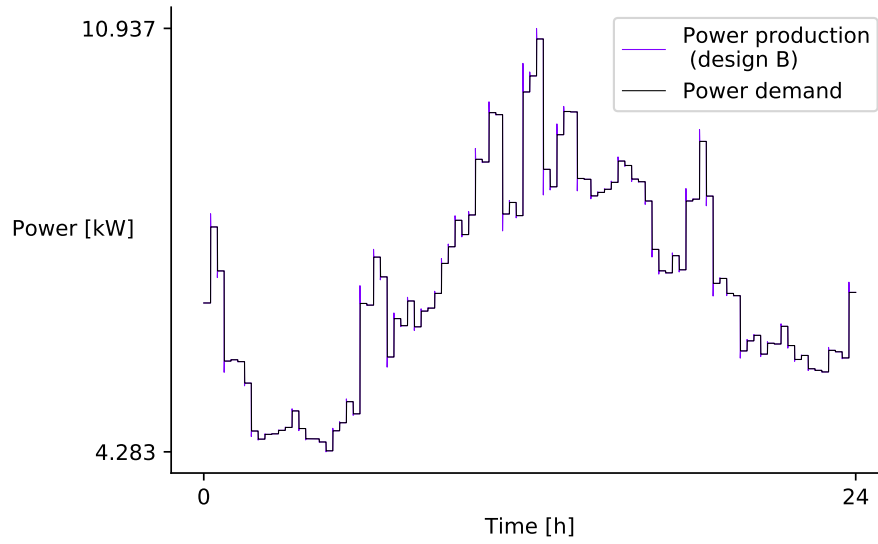


Figure 6.10: The power demand (black) and production (purple) for the average day of 2016 with the minimized average transient response.

C Buffer tanks mass content gap optimization results

C.1 Buffer tanks mass content gap and average over- and undershoots

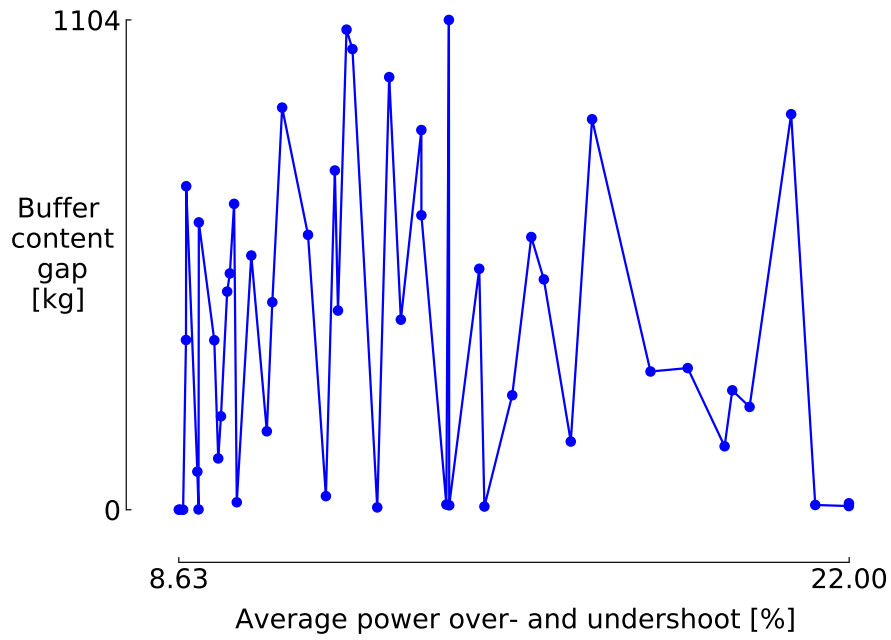


Figure 6.11: The buffer tanks mass content gap with respect to the average over- and undershoot for the 50 optimized designs.

C.2 Buffer tanks mass content gap and average transient response

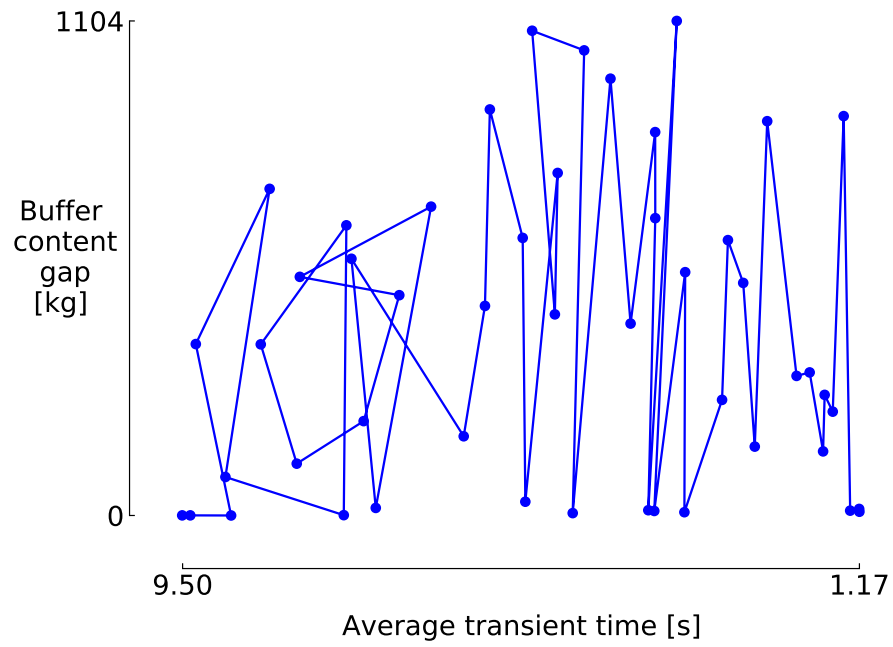


Figure 6.12: The buffer tanks mass content gap with respect to the average transient response time for the 50 optimized designs.

C.3 Buffer tanks mass content gap and power demand and production gap

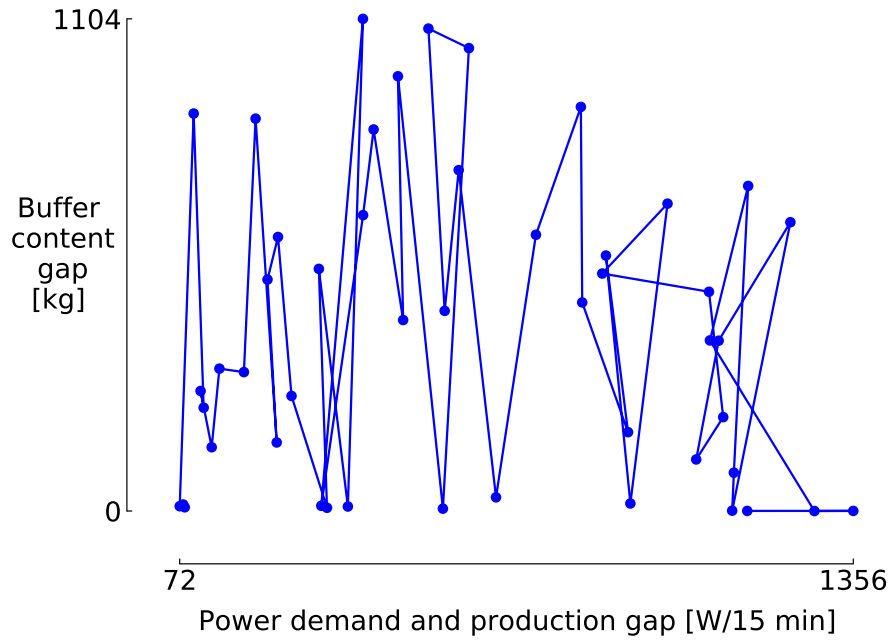


Figure 6.13: The buffer tanks mass content gap with respect to the power demand and production gap for the 50 optimized designs.

D The four optimization objectives with respect to the design variables.

D.1 Objective 1: average over- and undershoots

Ammonia cracker parameters

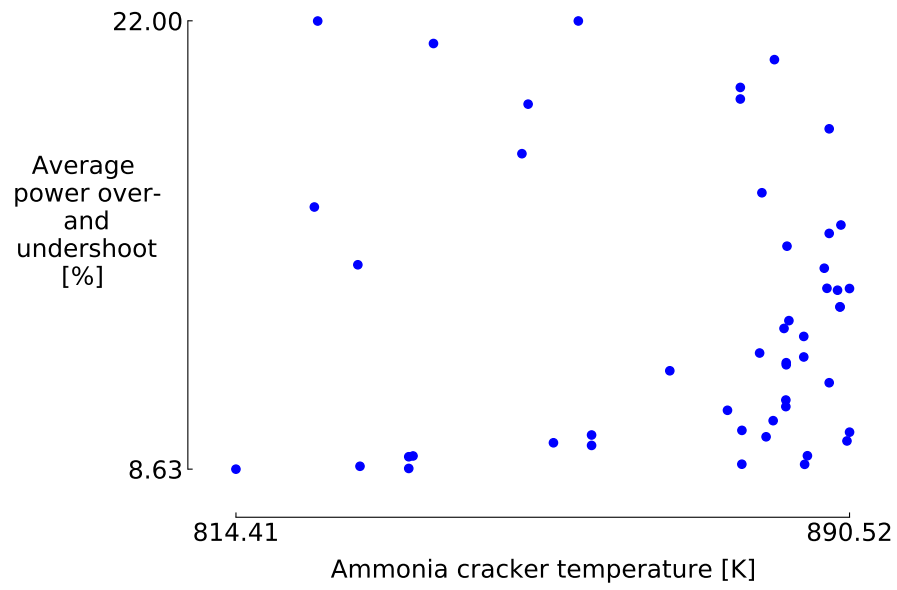


Figure 6.14: The average over- and undershoot with respect to the ammonia cracker temperature for the 50 optimized design.

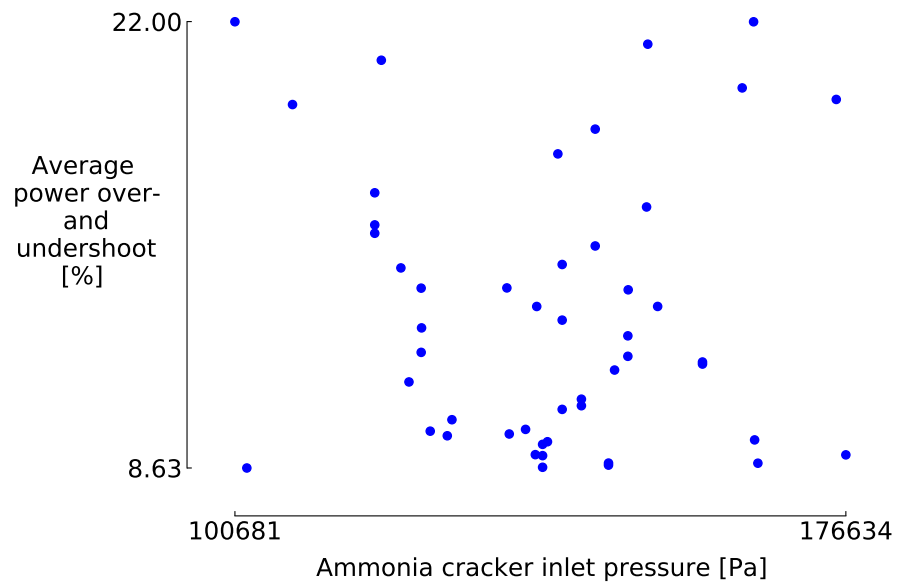


Figure 6.15: The average over- and undershoot with respect to the ammonia cracker inlet pressure for the 50 optimized design.

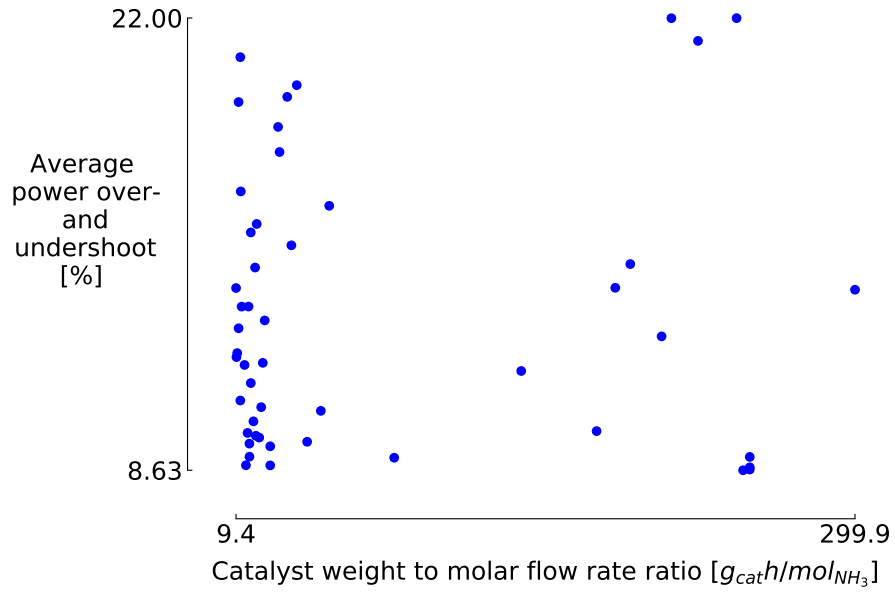


Figure 6.16: The average over- and undershoot with respect to the cracker catalyst weight to molar flow rate of ammonia ratio for the 50 optimized design.

Buffer tanks parameters

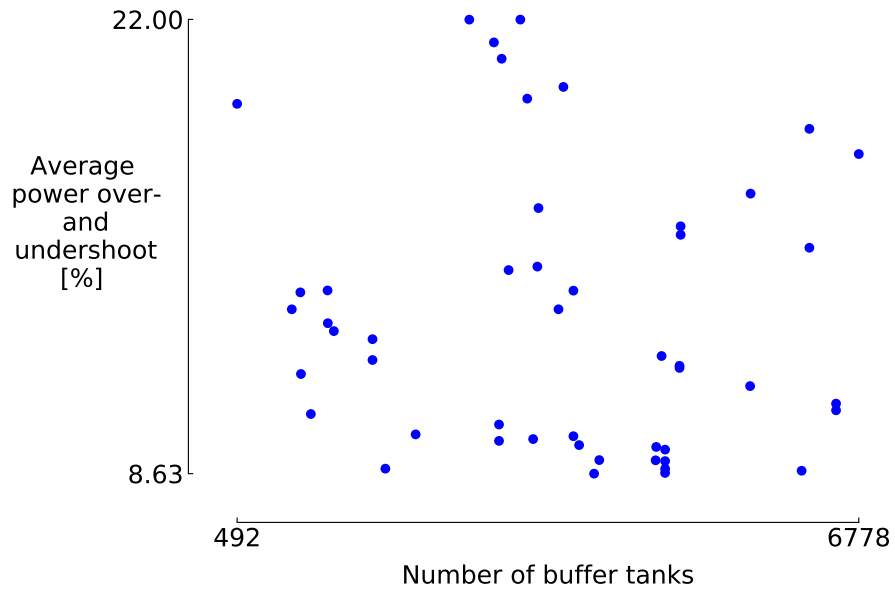


Figure 6.17: The average over- and undershoot with respect to the number of buffer tanks for the 50 optimized design.

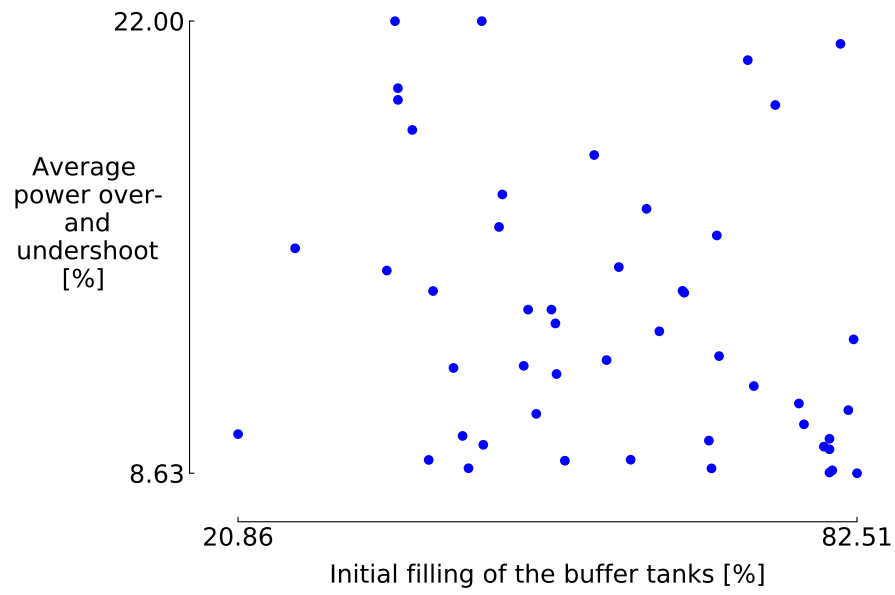


Figure 6.18: The average over- and undershoot with respect to the initial filling of the buffer tanks for the 50 optimized design.

PEMFC stack parameters

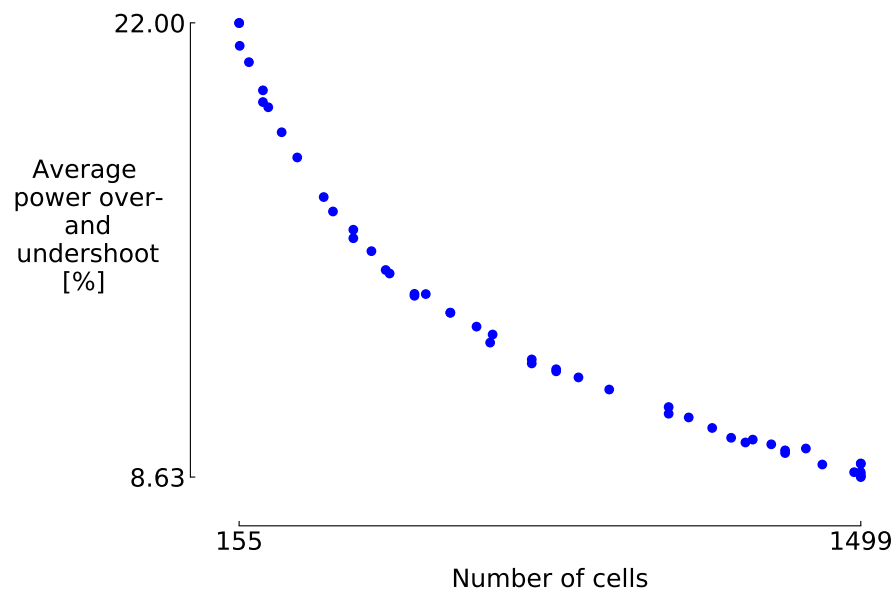


Figure 6.19: The average over- and undershoot with respect to the number of cells in the PEMFC stack for the 50 optimized design.

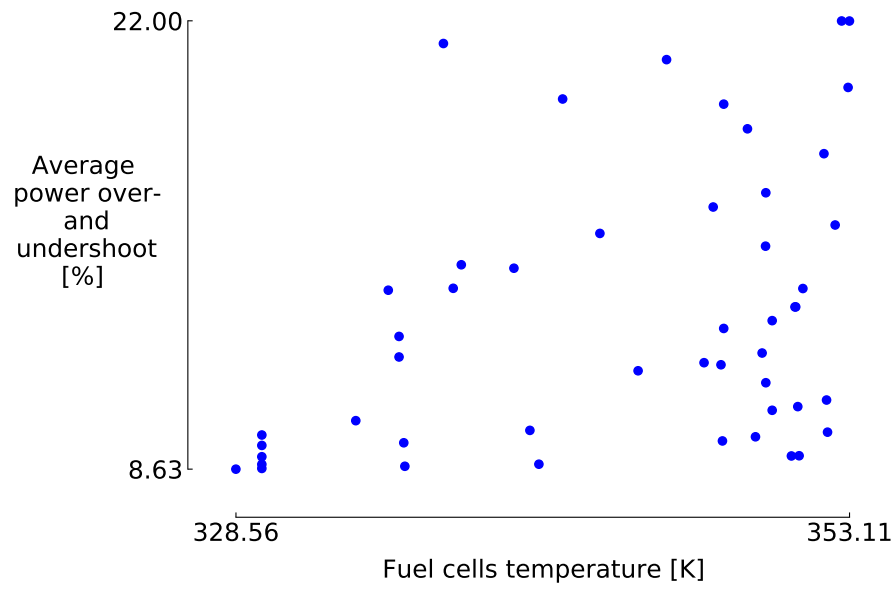


Figure 6.20: The average over- and undershoot with respect to PEMFC stack temperature for the 50 optimized design.

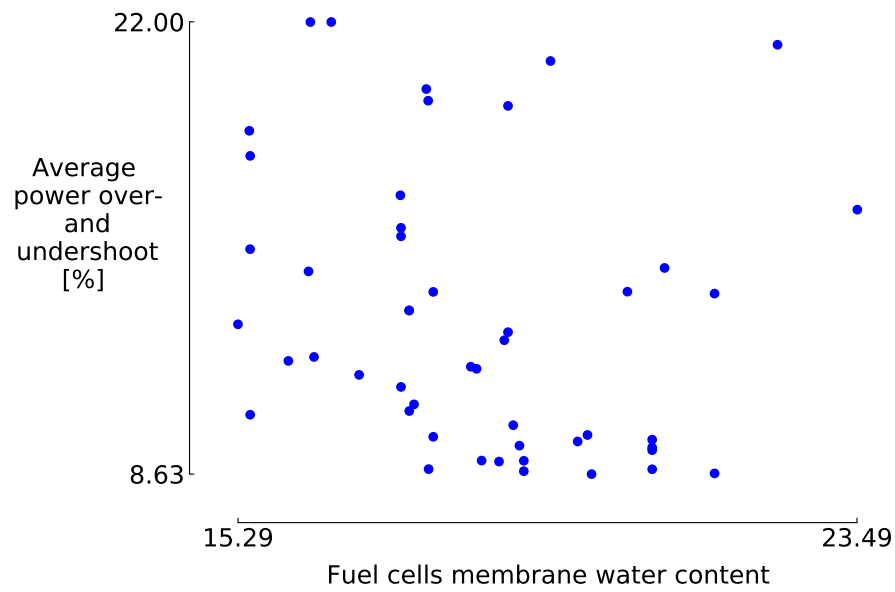


Figure 6.21: The average over- and undershoot with respect to the PEMFC stack membrane water content for the 50 optimized design.

D.2 Objective 2: average transient response times

Ammonia cracker parameters

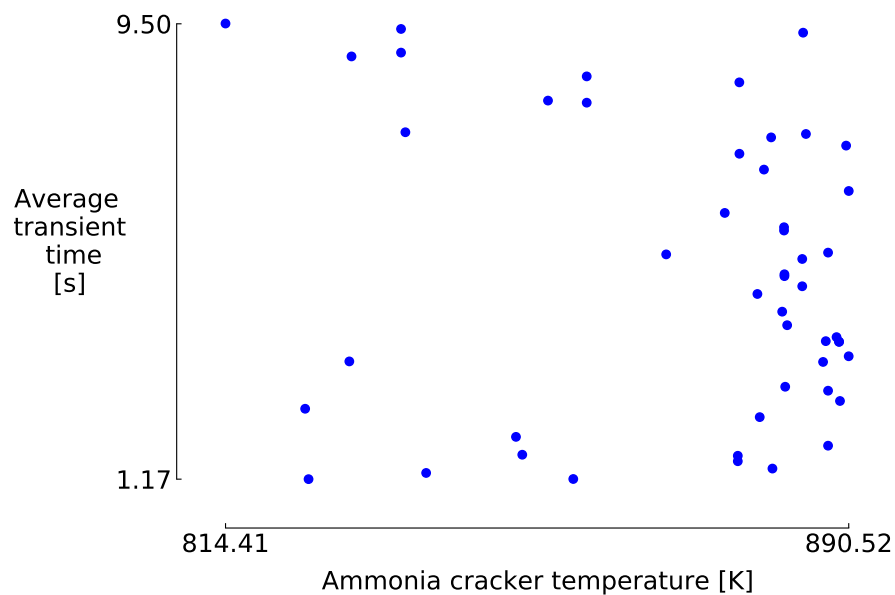


Figure 6.22: The average transient response time with respect to the ammonia cracker temperature for the 50 optimized design.

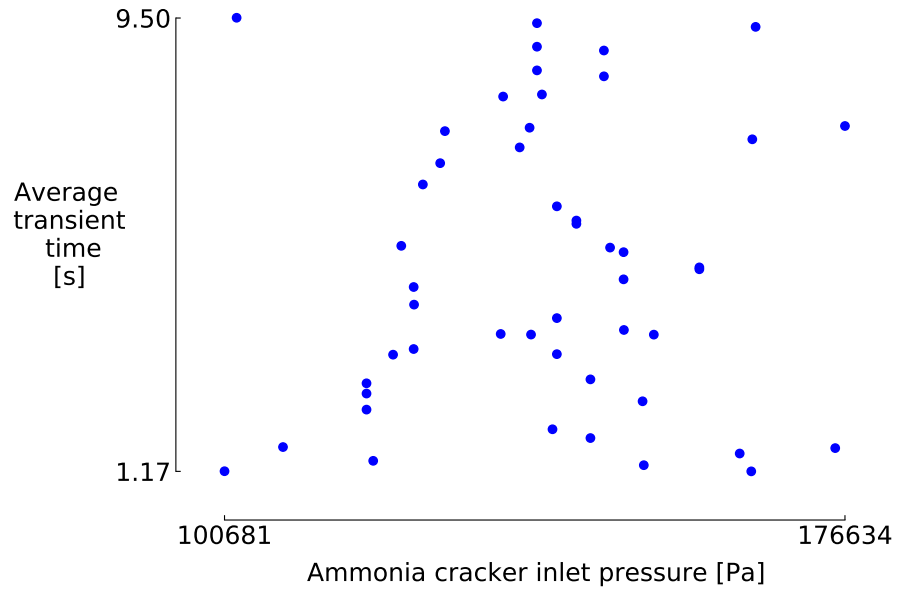


Figure 6.23: The average transient response with respect to the ammonia cracker inlet pressure for the 50 optimized design.

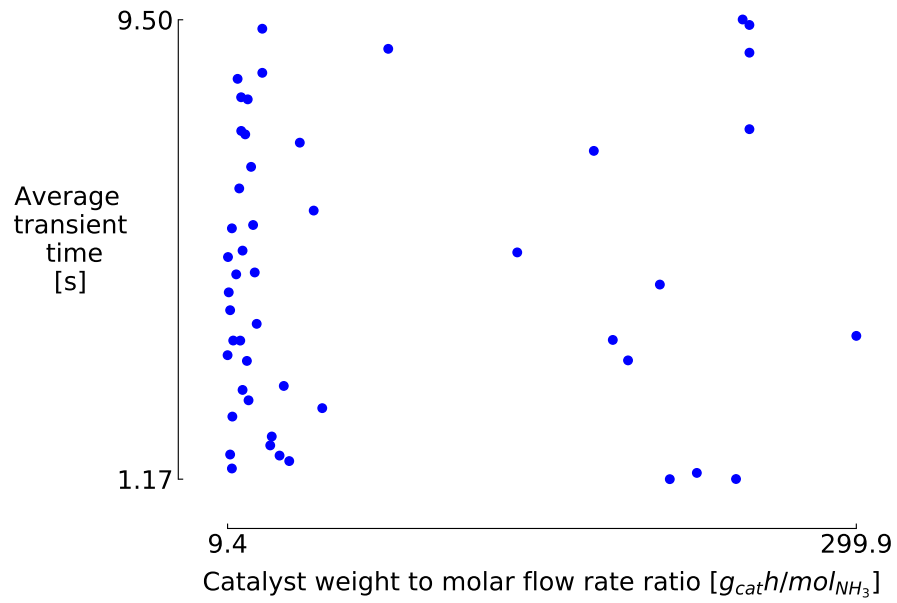


Figure 6.24: The average transient response with respect to the cracker catalyst weight to molar flow rate of ammonia ratio for the 50 optimized design.

Buffer tanks parameters

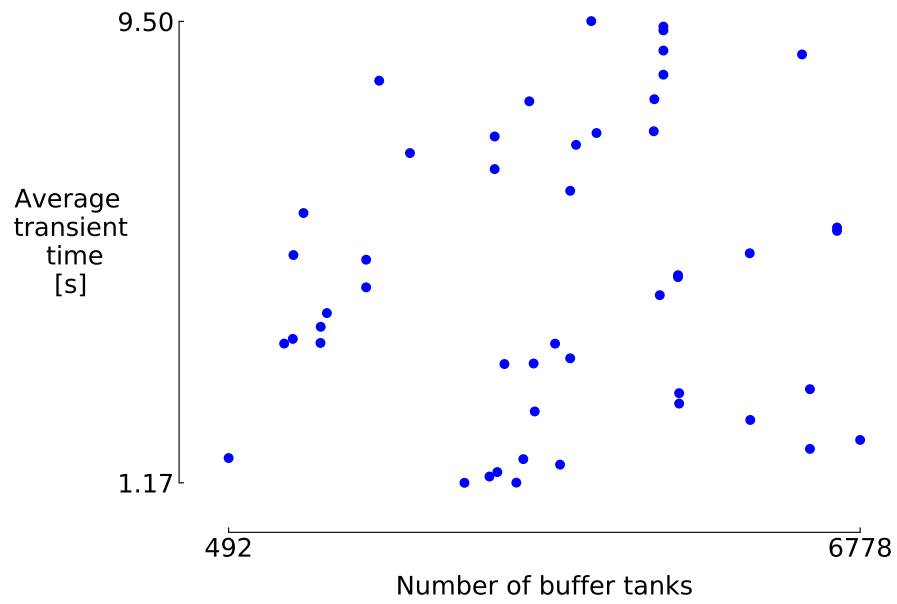


Figure 6.25: The average transient response with respect to the number of buffer tanks for the 50 optimized design.

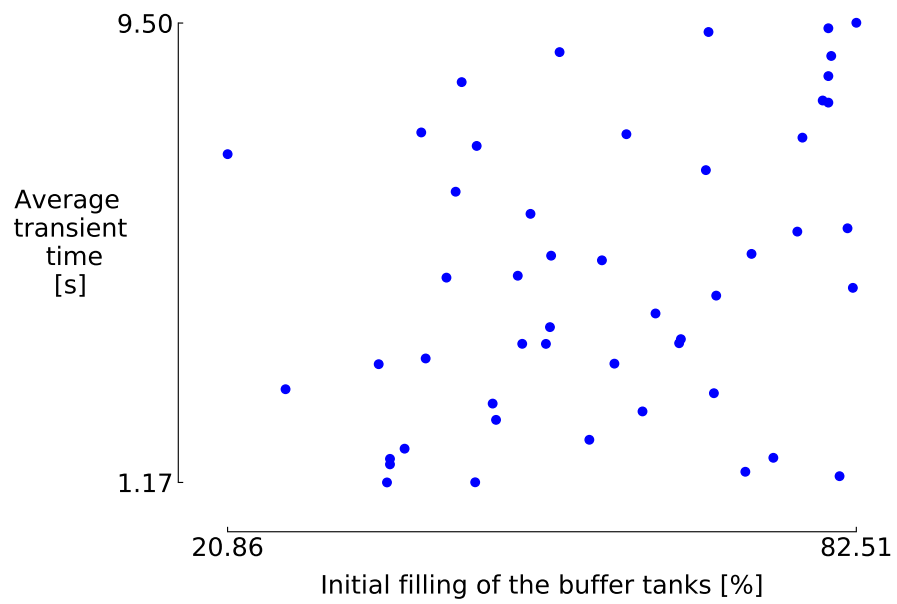
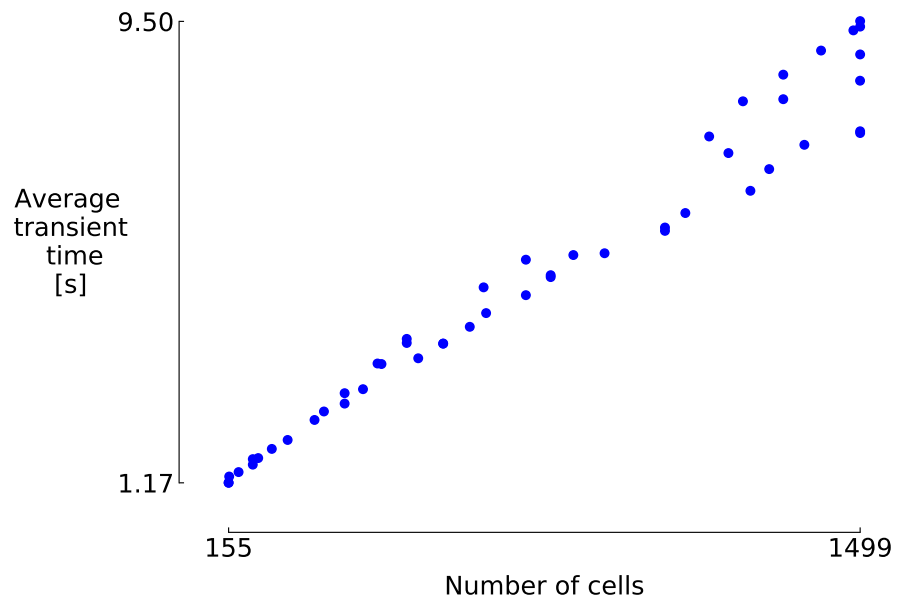


Figure 6.26: The average transient response with respect to the initial filling of the buffer tanks for the 50 optimized design.

PEMFC stack parameters



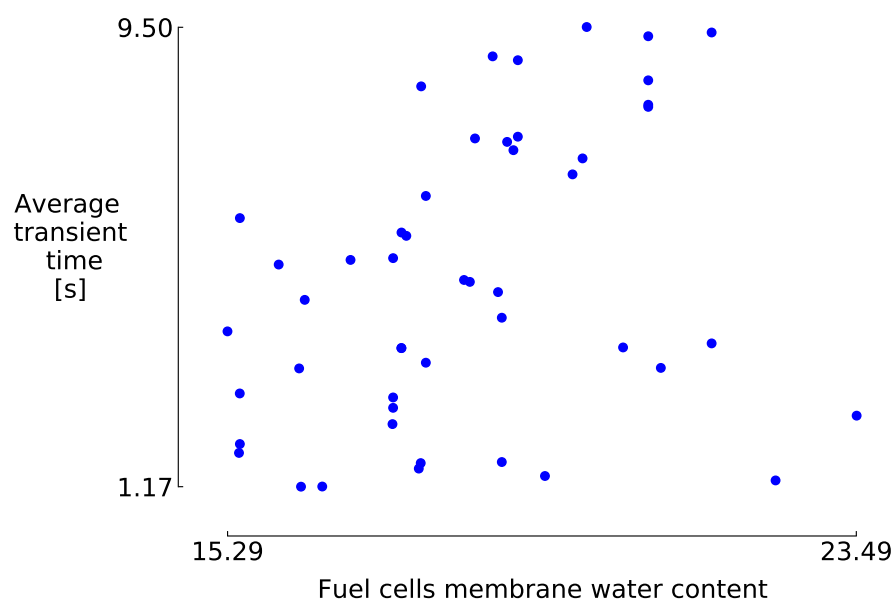


Figure 6.29: The average transient response with respect to the PEMFC stack membrane water content for the 50 optimized design.

D.3 Objective 3: buffer tanks mass content gap

Ammonia cracker parameters

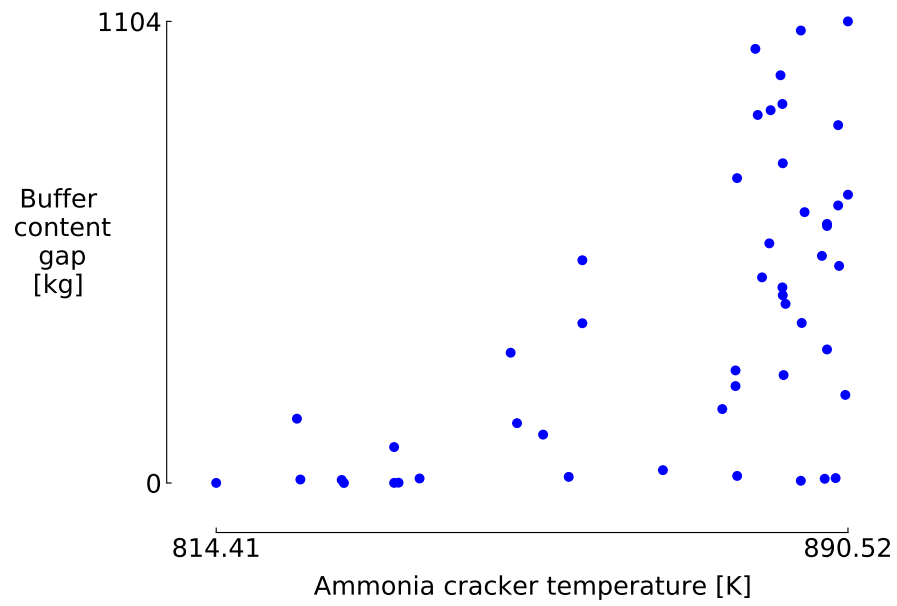


Figure 6.30: The buffer tanks mass content gap with respect to the ammonia cracker temperature for the 50 optimized design.

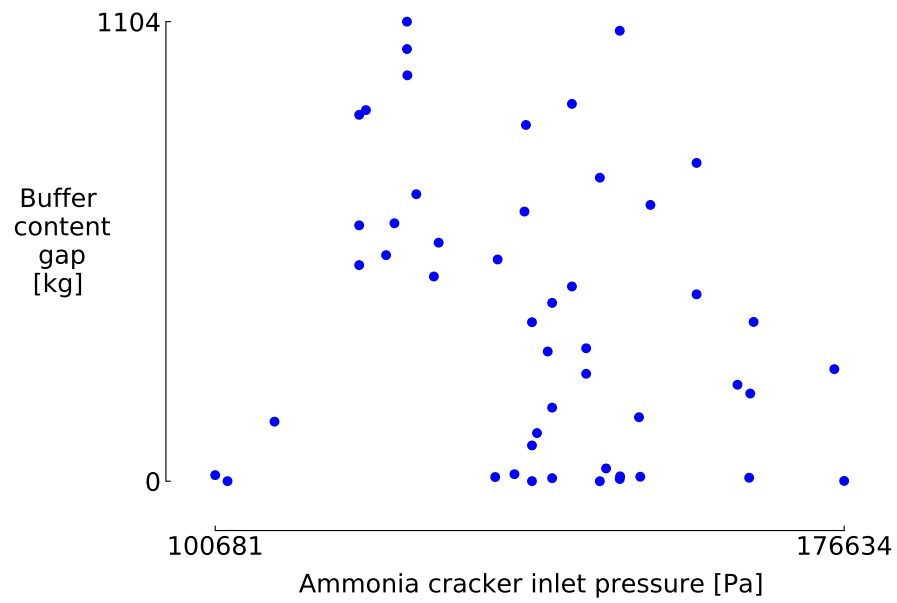


Figure 6.31: The buffer tanks mass content gap with respect to the ammonia cracker inlet pressure for the 50 optimized design.

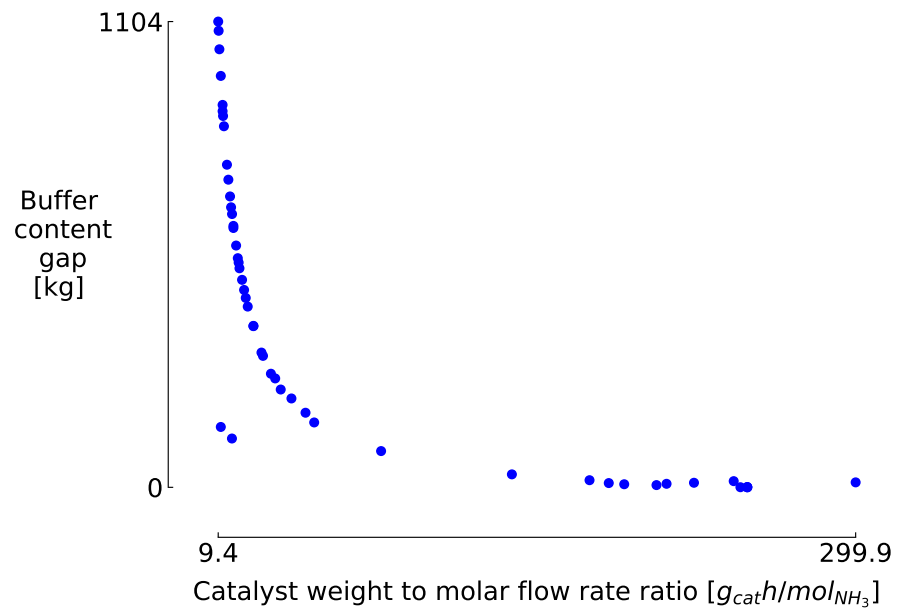


Figure 6.32: The buffer tanks mass content gap with respect to the cracker catalyst weight to molar flow rate of ammonia ratio for the 50 optimized design. A correlation is clearly appearing as the gap show a hyperbolic growth with a decrease of the ratio, and thus an increase of the molar flow rate of ammonia.

Buffer tanks parameters

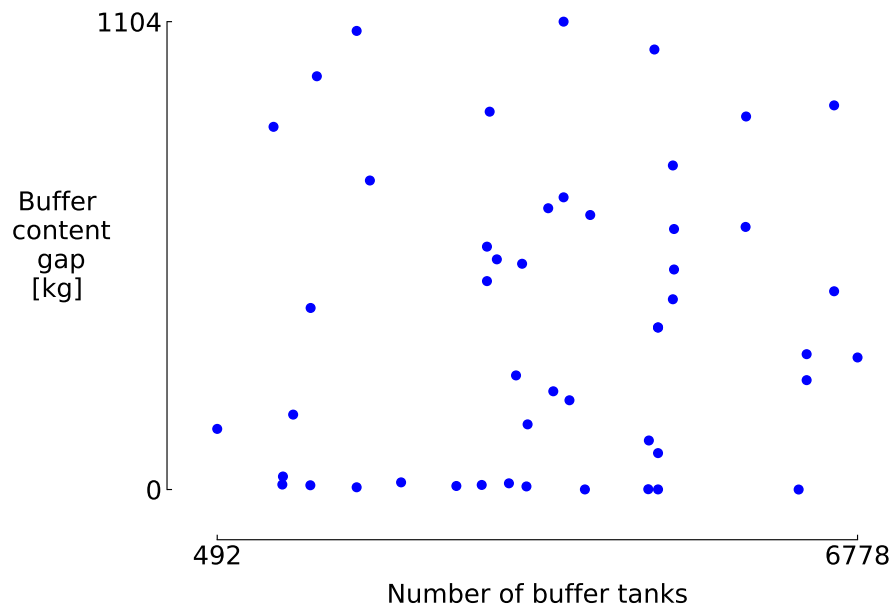


Figure 6.33: The buffer tanks mass content gap with respect to the number of buffer tanks for the 50 optimized design.

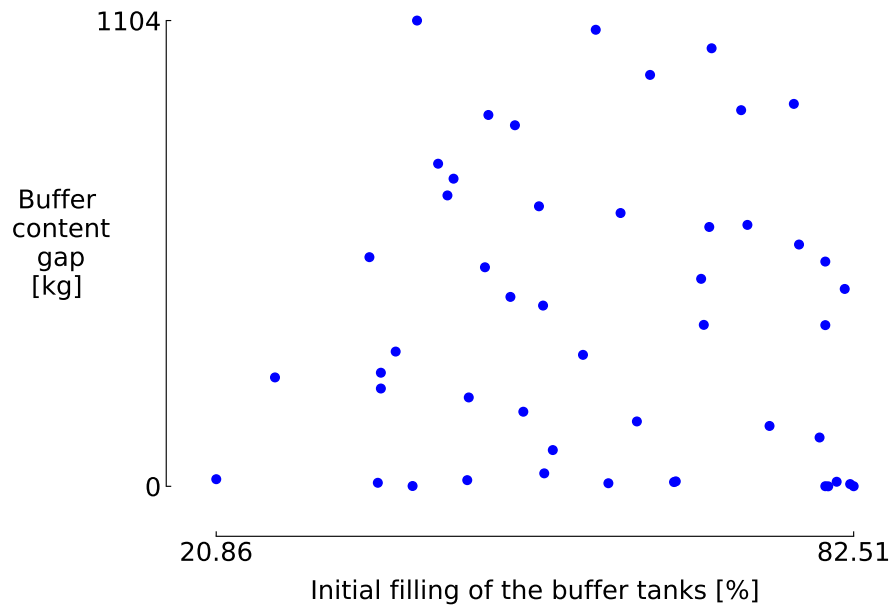


Figure 6.34: The buffer tanks mass content gap with respect to the initial filling of the buffer tanks for the 50 optimized design.

PEMFC stack parameters

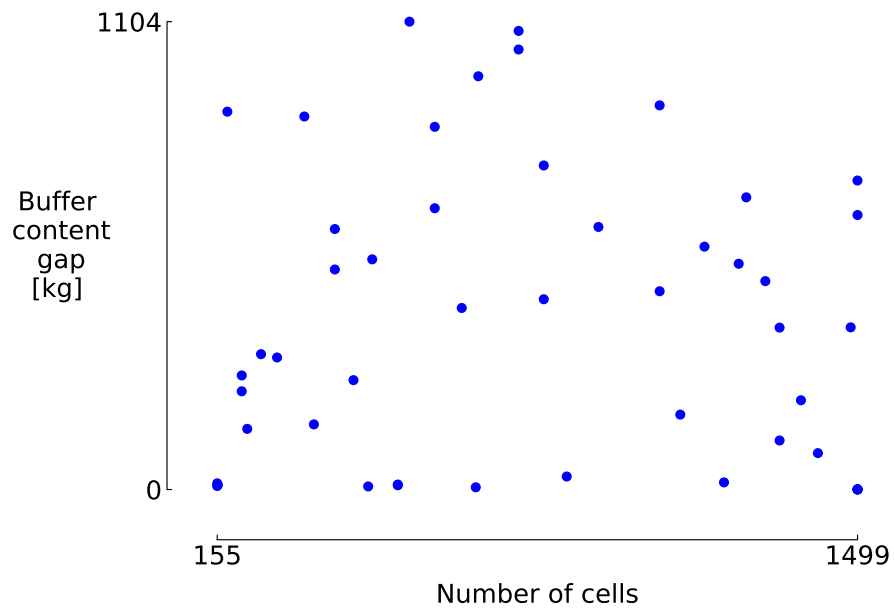


Figure 6.35: The buffer tanks mass content gap with respect to the number of cells in the PEMFC stack for the 50 optimized design.

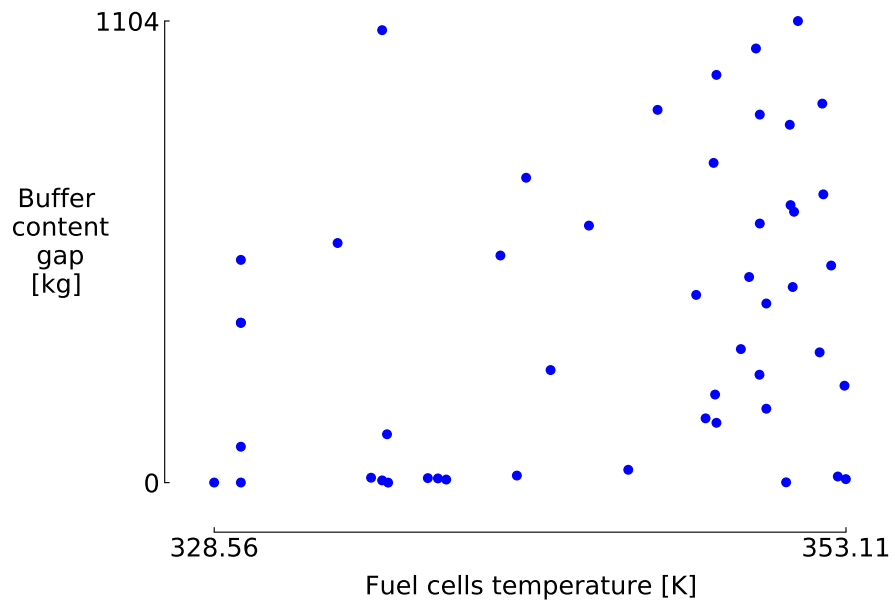


Figure 6.36: The buffer tanks mass content gap with respect to PEMFC stack temperature for the 50 optimized design.

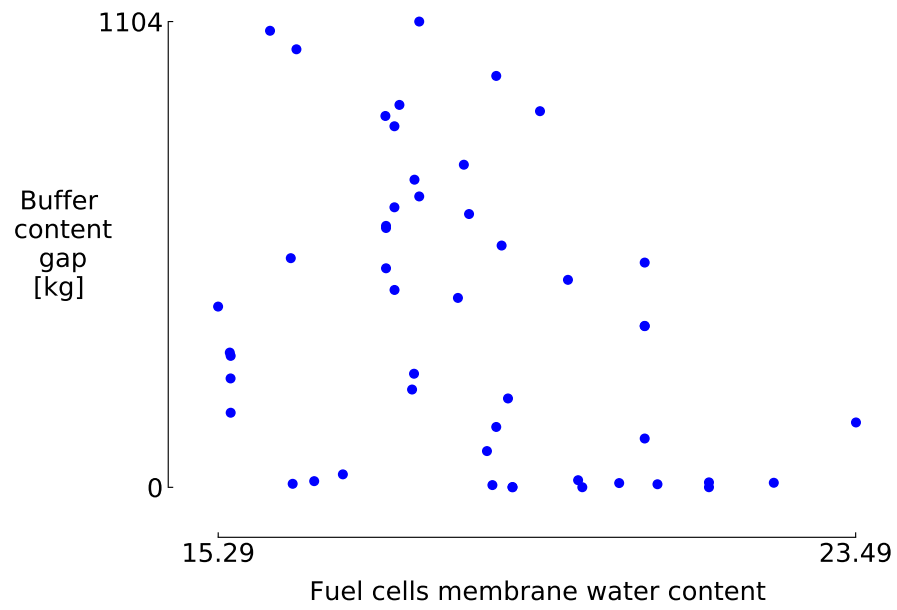


Figure 6.37: The buffer tanks mass content gap with respect to the PEMFC stack membrane water content for the 50 optimized design.

D.4 Objective 4: power demand and production gap

Ammonia cracker parameters

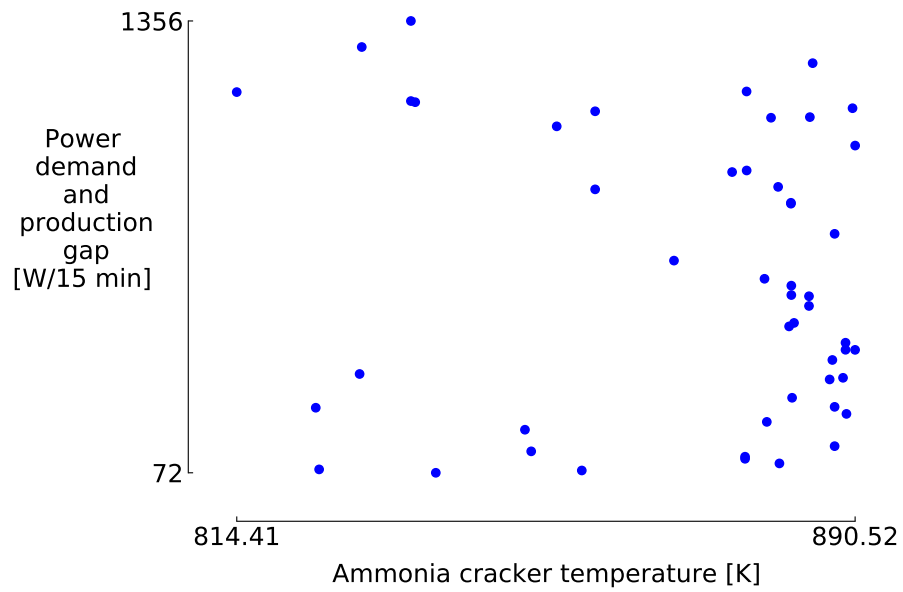


Figure 6.38: The power demand and production gap with respect to the ammonia cracker temperature for the 50 optimized design.

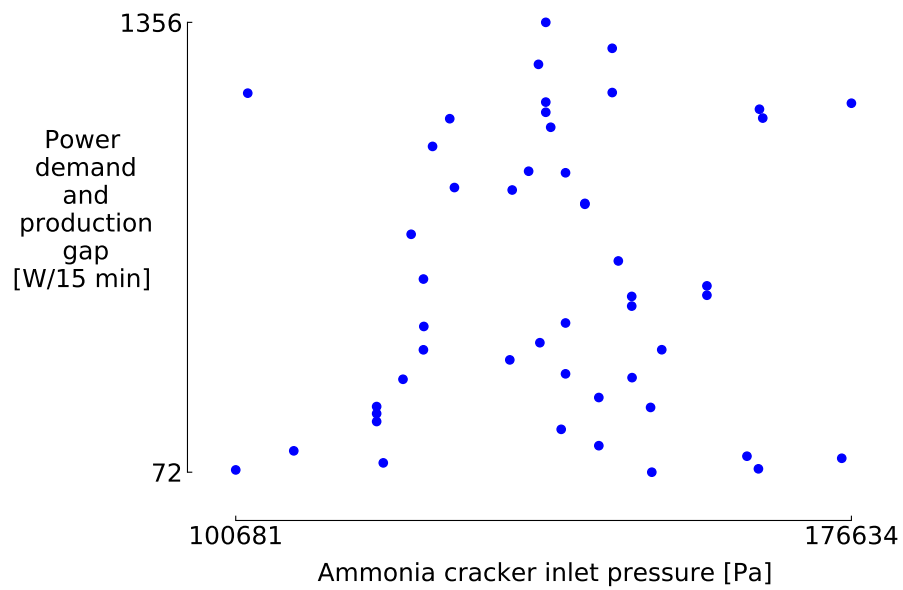


Figure 6.39: The power demand and production gap with respect to the ammonia cracker inlet pressure for the 50 optimized design.

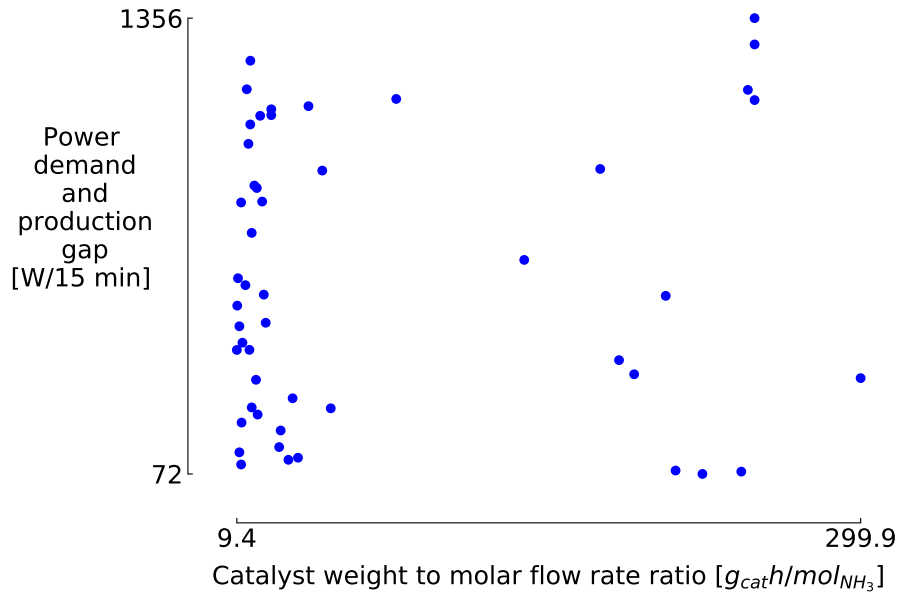


Figure 6.40: The power demand and production gap with respect to the cracker catalyst weight to molar flow rate of ammonia ratio for the 50 optimized design.

Buffer tanks parameters

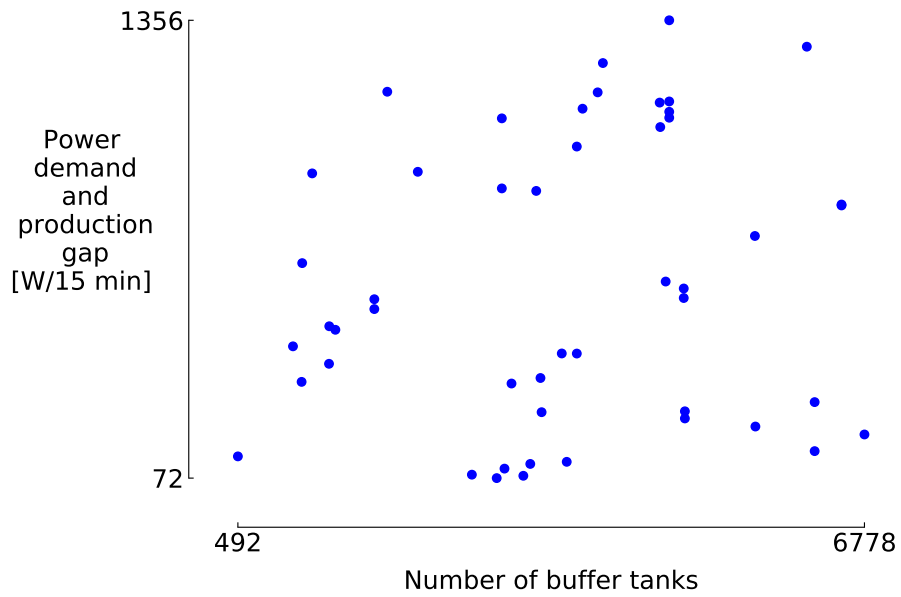


Figure 6.41: The power demand and production gap with respect to the number of buffer tanks for the 50 optimized design.

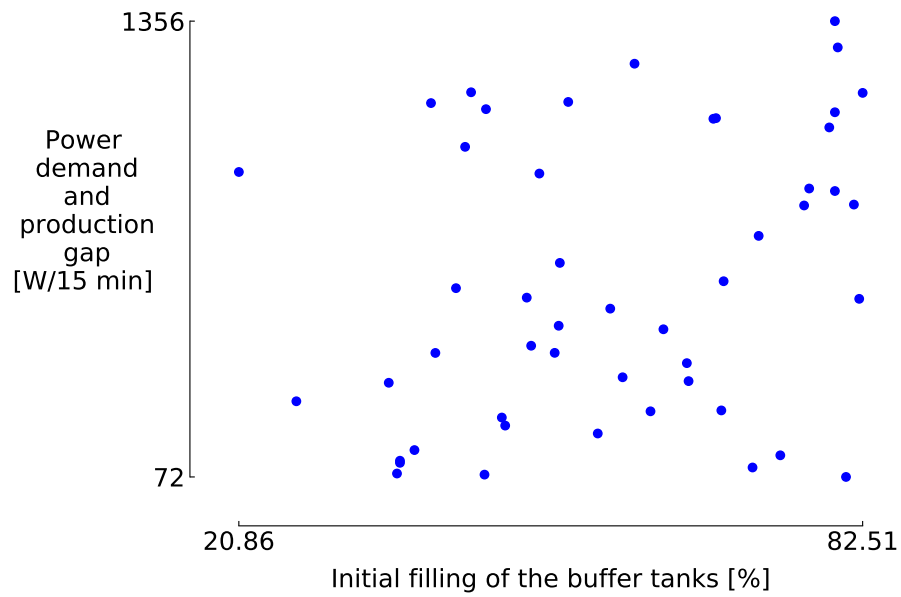


Figure 6.42: The power demand and production gap with respect to the initial filling of the buffer tanks for the 50 optimized design.

PEMFC stack parameters

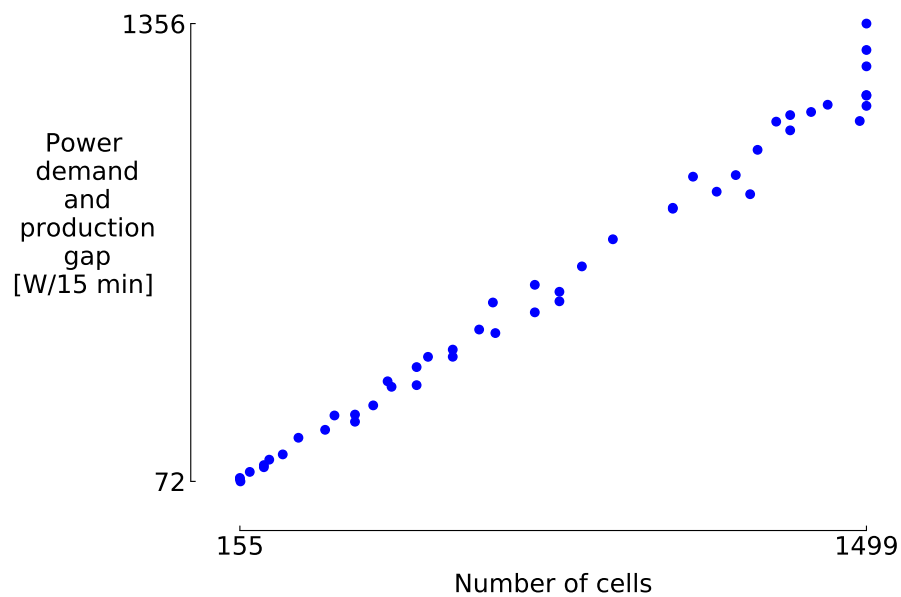


Figure 6.43: The power demand and production gap with respect to the number of cells in the PEMFC stack for the 50 optimized design. A linear correlation is clearly visible as the gap increases with the number of cells.

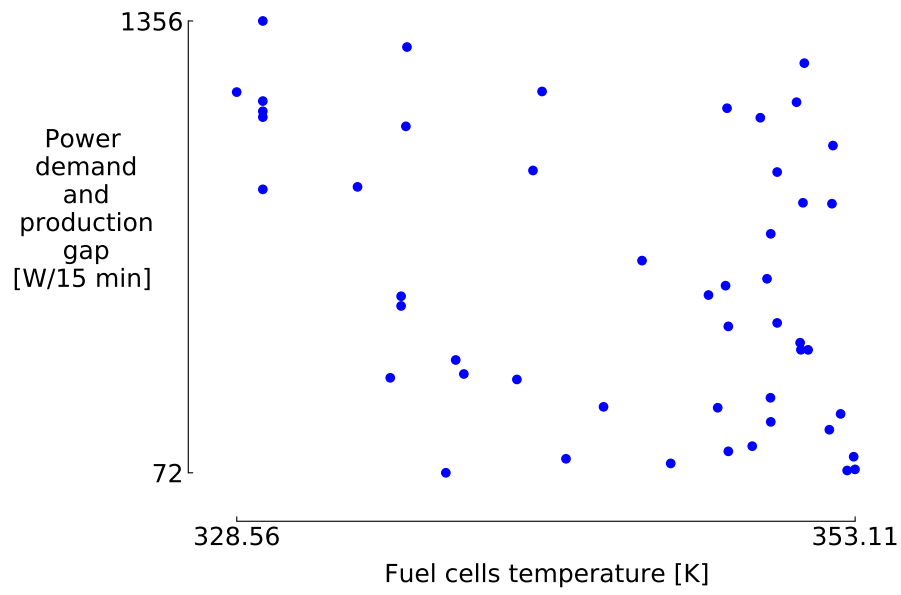


Figure 6.44: The power demand and production gap with respect to PEMFC stack temperature for the 50 optimized design.

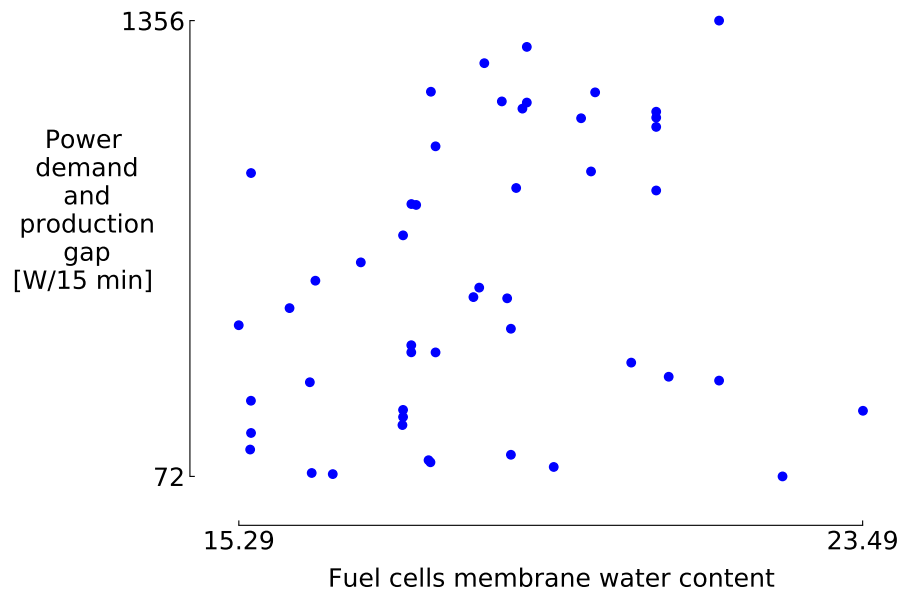


Figure 6.45: The power demand and production gap with respect to the PEMFC stack membrane water content for the 50 optimized design.

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