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Dynamics and Control of a Load Flexible Green Ammonia Plant

TESI DI LAUREA MAGISTRALE IN
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NTNU

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MASTER'S THESIS IN

CHEMICAL ENGINEERING - POLIMI

SUSTAINABLE CHEMICAL AND BIOCHEMICAL ENGINEERING - NTNU

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Abstract

The term 'green ammonia' is gaining in popularity as climate change concerns intensify. Currently, the production of ammonia contributes 1.8% to the global carbon emissions. The primary ammonia production method is the Haber Bosch process, which involves the reaction of hydrogen and nitrogen at high pressure and temperatures. The vast majority of the hydrogen utilized in this process, known as 'grey hydrogen', is derived from the carbon-intensive steam reforming of natural gas. A promising solution to decrease carbon dioxide emissions is to substitute grey hydrogen with 'green hydrogen', i.e., hydrogen derived from water electrolysis employing renewable energy, synthesizing what is referred to as 'green ammonia'. Green ammonia presents a wide range of applications, from traditional ones as fertilizers to more innovative and climate-driven ones, such as low-carbon fuel and energy storage.

A significant challenge associated with green ammonia production lies in the fluctuating nature of renewable energy sources. Consequently, ongoing research focuses on designing and operating flexible green ammonia plants capable of operating through different load changes to accommodate for hydrogen availability. Various licensors, such as Topsøe and Casale [1, 2], have suggested the feasibility of a green ammonia plant capable of sustaining load reduction down to 10/20% of the designed one.

In this thesis, a dynamic simulation of a green ammonia synthesis plant is conducted to investigate the impact of a load change on the system. Following the completion of the dynamic simulation, a control structure is evaluated and implemented to maintain the operating conditions within the desired ranges. The study analyses the results of a load change with different control structures. It is concluded that, confined to the intrinsic limitations posed by representing reality with a simulation, a flexible ammonia plant can be operated effectively, particularly in the case of gradual load changes.

Keywords: Green ammonia, Ammonia synthesis, Dynamic simulation, Control structure, Load changes, flexible load

Abstract in Italian

Termini come 'ammoniaca verde' (green ammonia in inglese) stanno aumentando la loro popolarità, a causa della crescente preoccupazione correlata al cambiamento climatico. Ad oggi, infatti, la produzione di ammoniaca è responsabile dell'1,8% delle emissioni globali di anidride carbonica. La sintesi di ammoniaca avviene tramite il processo Haber-Bosch, il quale prevede la reazione tra idrogeno e azoto ad alte temperature. La gran parte di idrogeno utilizzato in questa tipologia di processo proviene dal reforming del metano, un processo correlato ad alte emissioni di anidride carbonica. Per ridurre drasticamente tali emissioni, l'ammoniaca potrebbe essere prodotta a partire da idrogeno verde, proveniente dal processo di elettrolisi dell'acqua con corrente elettrica da fonti rinnovabili. L'ammoniaca verde, oltre a sostituire, almeno in parte, quella presente nell'industria odierna, può rappresentare un'alternativa come carburante low-carbon o essere utilizzata per trasportare e stoccare energia chimica.

La sfida principale associata a un eventuale impianto di ammoniaca verde risiede nella natura fluttuante delle fonti rinnovabili. Difatti, diversi studi si impegnano nella progettazione e operazione di impianti flessibili per la produzione di ammoniaca che possano adattarsi alla disponibilità di idrogeno verde. Alcuni dei più importanti fornitori di tecnologie chimiche, come Topsøe e Casale [1, 2], propongono soluzioni in grado di sostenere variazioni di carico fino al 10/20% del carico di progettazione.

Questa tesi presenta una simulazione dinamica del processo di produzione di ammoniaca, ottenuta con il software UniSim Design. Tale simulazione è stata utilizzata per studiare l'impatto che ha una variazione di carico sulle condizioni di processo. A completamento della simulazione è stato implementato un sistema di controllo per mantenere le condizioni operative nei limiti desiderati. Si può concludere che, nei limiti intrinseci che ha una simulazione nel descrivere accuratamente la realtà, un processo di produzione flessibile di ammoniaca può essere operato efficacemente, in particolare se la variazione di carico risulta graduale e non improvvisa.

Parole chiave: Ammoniaca verde, sintesi dell'ammoniaca, produzione di ammoniaca, simulazione dinamica, controllo, variazioni di carico.

Abstract in Norwegian

Termen 'grønn ammoniakk' (green ammonia, på engelsk) vinner popularitet ettersom bekymringene for klimaendringer øker. For øyeblikket bidrar produksjonen av ammoniakk med 1.8% av de globale karbonutslippene. Den primære ammoniakkproduksjonsmetoden er Haber-Bosch-prosessen, som innebærer reaksjonen av hydrogen og nitrogen under høyt trykk og temperaturer. Størstedelen av hydrogenet som brukes i denne prosessen, kjent som 'grått hydrogen', kommer fra karbonintensiv dampreforming av naturgass. Et lovende alternativ for å redusere karbondioksidutslipp er å erstatte grått hydrogen med 'grønt hydrogen', det vil si hydrogen produsert fra elektrolyse av vann ved hjelp av fornybar energi, og dermed produsere det som kalles 'grønn ammoniakk'. Grønn ammoniakk har et bredt spekter av bruksområder, fra tradisjonelle bruksområder som gjødsel til mer innovative og klimadrevne bruksområder som lavkarbonbrensel og energilagring.

En betydelig utfordring knyttet til produksjon av grønn ammoniakk er at fornybare energikilder er variabel av natur. Som et resultat fokuserer pågående forskning på å designe og drive fleksible grønne ammoniakfabrikker som er i stand til å operere gjennom ulike belastningsendringer for å tilpasse seg tilgjengeligheten av hydrogen. Forskjellige lisensgivere, som Topsøe og Casale [1, 2], har foreslått løsninger for å opprette en grønn ammoniakfabrikk som er i stand til å opprettholde en belastning på 10/20% av den designete belastningen.

I denne avhandlingen er det gjennomført en dynamisk simulering av en grønn ammoniakksyntesefabrikk for å undersøke virkningen av en belastningsendring på systemet. Etter fullføring av dynamiske simuleringer, er en reguleringsstruktur evaluert og implementert for å opprettholde driftsbetingelsene innenfor ønskede områder. Studien analyserer resultatene av en belastningsendring med ulike reguleringsstruktur. Det konkluderes med at, begrenset av de iboende begrensningene som stilles av representasjonen av virkeligheten med en simulering, kan en last-fleksible ammoniakfabrikk drives effektivt, spesielt ved gradvise belastningsendringer [3].

Nøkkelord: Grønn ammoniakk, Ammoniaksyntese, Dynamisk simulering, Reguleringsstruktur, Lastendringer

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1 | Introduction

With increasing concerns over climate change, low carbon goals are set from international conferences and agreements, from the Kyoto Protocol to the Paris Agreement. Researchers and industry are therefore working towards greener and more sustainable means of maintaining society's established living habits while decreasing its emissions. It is in this landscape that low-carbon compounds, such as green hydrogen and green ammonia, find a flourishing habitat. Hydrogen is one of the most quoted fuels to replace fossil-based ones, as a clean and dense energy carrier. However, regardless of its strengths, hydrogen is highly flammable, which raises diverse safety concerns around hydrogen-based low-carbon solutions. Ammonia, on the other hand, beyond its use in the green fertilizers industry, can be employed to transport and store hydrogen, serving as a safe hydrogen carrier, and, in some cases, as a fuel itself, helping in the transition from fossil fuels [4, 5].

Ammonia production began in the 19th century and has increased steadily ever since. Currently, the vast majority of ammonia produced, 85%, is employed in the fertilizer industry for the production of nitrogen-based fertilizers, essential for plant growth. Therefore, this production is closely linked to the agricultural sector, correlating the growth rate of ammonia synthesis with that of the world's population, and shaping the society as we know it today [6, 7].

The main ammonia production process, the Haber Bosch, is a catalytic process in which hydrogen and nitrogen react at high pressure and temperature to form ammonia [6]. Based on the hydrogen employed, the overall emissions linked to the production vary greatly. Currently, the hydrogen used is mainly grey hydrogen, which is produced from natural gas reforming. This results in ammonia production being responsible for about 1.8% of worldwide carbon dioxide emissions. Therefore, ammonia production decarbonization is of fundamental interest. Figure 1.1 reports the predicted decrease of CO₂ emission in ammonia production, according to the International Energy Agency [8]. In the figure, three scenarios have been considered: stated policies, sustainable development goals, and net zero by 2050 goals. It is clear that, both in the sustainable development scenario and in the net-zero by 2050 scenario, ammonia production needs to be significantly decarbonized.

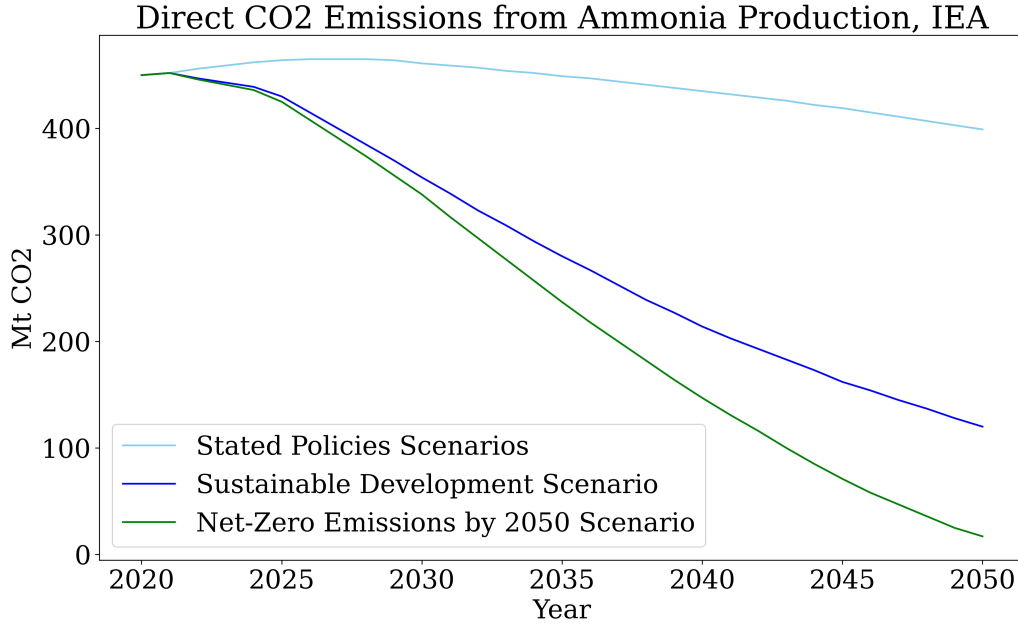


Figure 1.1: Direct CO₂ emissions from ammonia production, 2020-2050, International Energy Agency [8].

In this scenario, green ammonia, which is ammonia produced from green hydrogen and nitrogen, finds an important role. Green hydrogen is produced through water electrolysis in which renewable energy is employed. However, there are significant challenges in using green hydrogen in ammonia production. The primary one lies in the fluctuating nature of renewable energies, which leads to fluctuating hydrogen production rates. Traditional ammonia plants operate at a fixed rate and therefore require a fixed feed flow of hydrogen and nitrogen. The ammonia plants in which hydrogen is derived from renewable energy, such as solar or wind power, must deal with the variability of these sources, which are highly dependent on the weather conditions. One approach to this challenge is relying on energy storage to ensure a constant hydrogen input. The other approach is to design and operate flexible ammonia plants. Several licensors claim to offer ammonia synthesis plants able to sustain operations down to 10/20% the nominal load [1, 2, 9]. The benefits of a flexible plant compared to hydrogen storage have been analyzed by licensors such as Casale [9, 10], concluding that their technology can greatly reduce the capital investment, eliminating the need of hydrogen storage. Beyond merely economic considerations, it is important to underline that hydrogen storage, especially for large-scale plants, involves significant safety risks due to hydrogen's high flammability [9].

In this thesis, a dynamic simulation of a flexible ammonia plant with a nominal production of 10000 kg/h is conducted with the software UniSim Design R492. Simulations are highly useful to understand and visualize plant operations. Steady-state simulations, commonly

adopted in process design, provide fundamental information on how the process runs at a steady state, i.e., without time dependence. In this case, steady-state simulations about ammonia synthesis at different loads have been conducted in a previous project [11]. Dynamic simulations, on the other hand, are particularly valuable for studying time-dependent behaviors such as start-ups and shutdowns, unusual disturbances, and planned transitions [12]. In the case of a dynamic ammonia plant, the hydrogen inlet will be adjusted based on its availability, through planned transitions, which makes dynamic simulation results particularly instructive. In this project, the dynamic simulation is used to study the operability of a flexible load green ammonia plant. The load is decreased down to 20% of the nominal load, where nominal refers to the designed load. Since one of the fundamental aspects of a dynamic ammonia plant is ensuring proper control so that the transition between different loads can occur smoothly, a control structure that considers both the temperature and pressure in the system is studied.

2 | Theory and Background

This chapter begins with an overview of green ammonia production. It then describes assumptions and results obtained in the steady state simulations conducted in a previous work [11]. It ends with an introduction to dynamic simulation and a literature review on different control structures for ammonia synthesis plants.

2.1. Ammonia Synthesis

Green ammonia synthesis is schematized in Figure 2.1 [4]. It mainly comprises the production of synthesis gas, i.e. hydrogen and nitrogen, and its conversion into ammonia. Traditionally, the synthesis gas is produced through two-stage methane reforming. Being this a highly carbon-intensive process, other routes are being explored. In green ammonia, hydrogen is produced through water electrolysis employing renewable energy, such as wind or solar, while nitrogen is obtained through an air separation unit (ASU)[4].

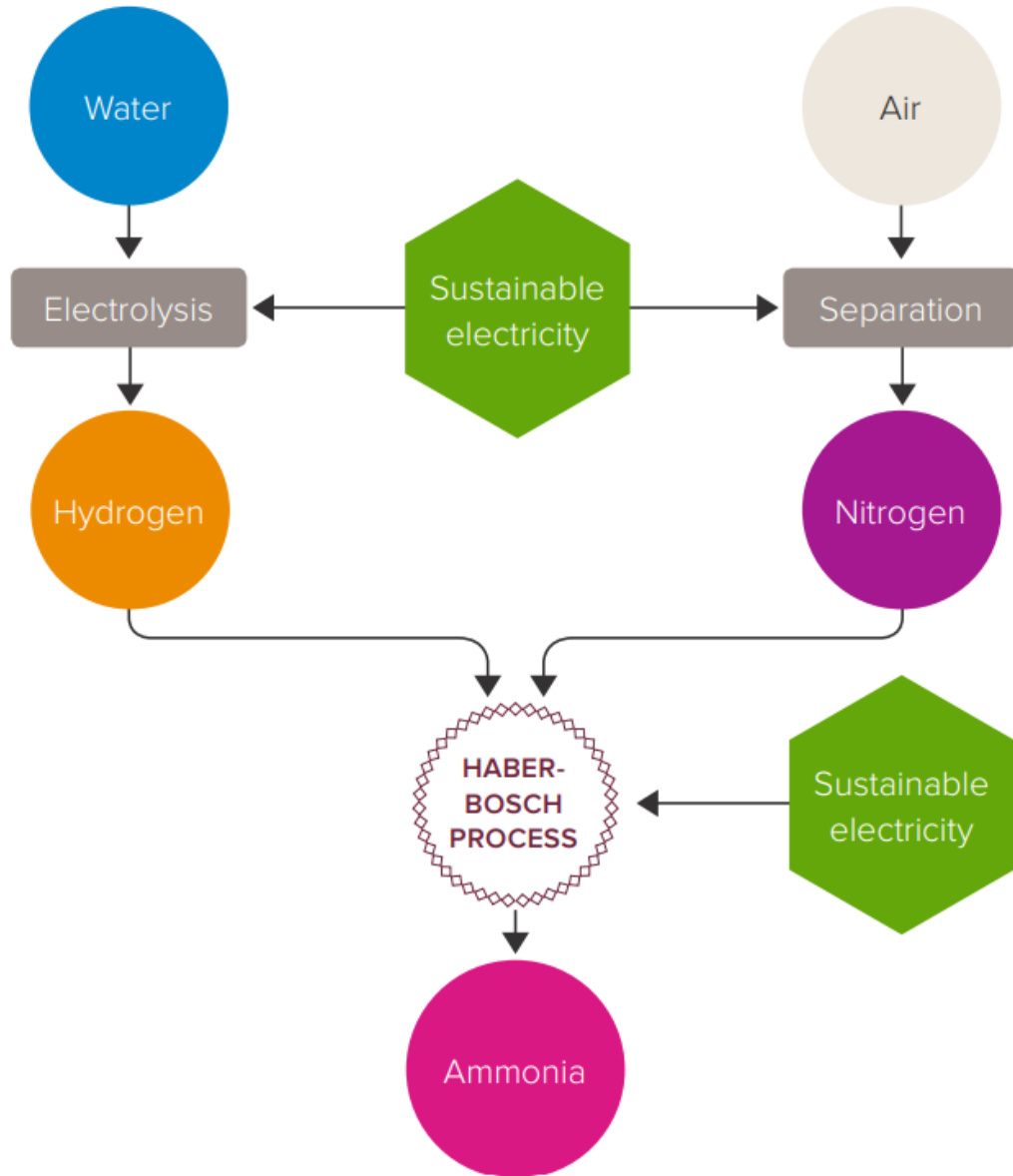


Figure 2.1: Schematised green ammonia production [4].

2.1.1. Hydrogen and Nitrogen Production

To produce green ammonia, both hydrogen and nitrogen have to be produced through green technologies. Nitrogen is produced through an air separation unit (ASU), which can be a cryogenic air separation or a pressure swing absorption unit. In the first case, the air temperature is reduced so that its components can be separated using different distillation columns. In the second, a column with an adsorbent material is used to separate the air components. The adsorbent material affinity towards one of the components is exploited to trap the component in the column, which will then be released by a reduction of pressure [13].

The hydrogen employed is produced via electrolysis. Electrolysis involves the passage of current through an electrolyte cell where water is present. This will lead to two reactions: the hydrogen and oxygen evolution, which happen, respectively, at the cathode and anode of the electrolyte cell. When the electricity used for this process is renewable energy, the hydrogen produced is called 'green hydrogen' [14]. Today, a small percentage of hydrogen is produced using water electrolysis (4%), and when it is, it is usually in the chlor-alkali industry [15]. The electrolysis processes are differentiable based on the electrolyte used. The two that, as of today, are commercially available are alkaline water electrolysis and the polymeric electrolyte membrane (PEM) water electrolysis. To choose the right technology, it is important to consider the specific requirements of the process. More specific information and comparison between the technologies can be found in literature [15], including which technology is more economically feasible specifically for green ammonia production [16, 17]. Whichever option may be more advantageous in the specific condition, a fluctuating energy input will result in an unstable hydrogen production. The fundamentals of green energy sources and their respective fluctuations are given in the next paragraph.

Renewable Energy Fluctuations

Renewable energy is energy produced from natural sources, that can regenerate faster than they are consumed [18]. Renewables are considered to be fundamental in the energy transition, as they could allow society as we know it to maintain its living standards while reducing its dependence on fossil sources. Moreover, with the current geopolitical instabilities, energy independence is becoming more appealing, and, in contrast to natural reservoirs such as oil and gas, renewables are not region-specific. Therefore, a great number of investments are focusing on renewables, and their expansion is forecast to be as never before in the near future [19].

The most likely renewable energy to be used in green ammonia production is either wind or solar power, as most of the hydropower energy produced is already in use. In Norway, particular attention is given to offshore wind power production [8, 20]. The fundamentals of these two sources are therefore given in the next paragraphs.

Solar Energy is based on the conversion of solar radiation into electricity through photovoltaic panels or mirrors that concentrate the radiation. Even if it is not the most exploited, it is the most abundant renewable energy source and it is forecast to be more and more exploited, due to low carbon goals and large availability. The electricity production depends on the radiation intensity, which changes depending both on the time of the day

and period of the year [21].

Wind Energy is based on the use of wind turbines to convert the kinetic energy in the moving air into electrical energy. It is the second source of renewable energy in Norway, after hydropower [20]. The technology has been used for decades, and, in the last years, it has undergone substantial growth due to the low carbon goals. The energy production directly depends on the velocity of the wind. For this reason, the optimal location for wind turbines is usually somewhere remote, far from construction which can hinder the wind. Therefore, offshore wind production is increasing its attractiveness, as it has tremendous potential [18]. The dependence on the wind speed however has its downsides: the more unstable the velocity is, the more the energy produced will fluctuate. An example of a 24-hour variation is reported in Figure 2.2 [22], where it is possible to observe that this energy source is far from stable.

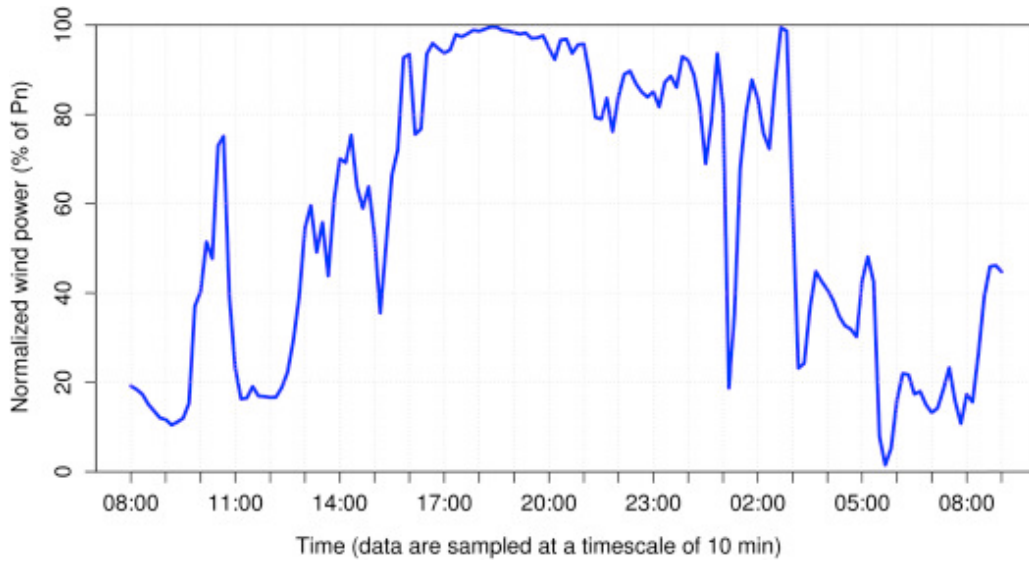
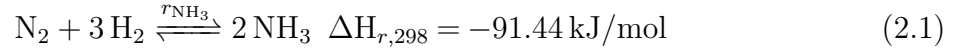


Figure 2.2: An example of daily variation of wind energy [22].

2.1.2. The Haber Bosch Process

The principal way of synthesizing ammonia is the Haber Bosch process. Invented by Fritz Haber and Carl Bosch in the 1910s, it is regarded as one of the greatest achievements in chemical engineering. Firstly, ammonia is the basis for the production of nitrogen-based fertilizers, which are essential in sustaining food production for the growing world population. Moreover, ammonia synthesis was the first chemical process to be conducted at high pressure, paving the road for other major productions [6].

The equation at the heart of the process is Equation 2.1:



It is a highly exothermic reaction with a decrease in the number of moles. This means, according to the Le Chatelier principle, that the reaction is thermodynamically favored by low temperatures and high pressures. The temperature, however, is a compromise between thermodynamics and kinetics: if too low, the reaction kinetic is hindered. Typical operating conditions have a temperature range of 675 K - 770 K. Haber was the first to understand that high pressures with an efficient catalyst could be used to produce ammonia. Today, ammonia synthesis is carried out at a pressure of 100-250 atm and about 675 K - 770 K. Even with these features, the conversion per pass does not surpass 30%, which makes it necessary to recycle the unreacted gas [6].

Catalyst and Reaction Kinetics

The catalyst is at the heart of the process, as it is required to operate the reaction at a lower temperature, which is fundamental for thermodynamic reasons, as explained above. The catalyst used is a multi-promoted iron-based catalyst which was first formulated by Haber, Bosch, and Mittash at BASF, in a project in which they tested more than 6500 catalysts [6]. Research into different catalyst formulations remains ongoing, therefore the specific formulation varies depending on the specific catalyst provider. Typically, the base is iron-promoted with non-reducible oxides. Promoters can be divided into structural promoters, such as Al_2O_3 , which have the function of stabilizing the catalyst, and electronic promoters, such as the oxides, which increase the catalyst activity. Normally, the ammonia catalyst is designed to optimally operate between 380-550 °C and at pressures between 14-45 MPa. However, when the process requires it, the formulation can be adjusted so that the allowed temperature is higher, for instance by increasing the structural promoters [7, 23]. In the case of green ammonia synthesis, particular attention should be given to the catalyst temperature. Operating at lower loads will increase the residence time in the reactor and, consequently, overheating of the catalyst can occur [24].

The kinetic model. In the last century, the need to describe ammonia synthesis and study the process has resulted in different kinetic expressions that more or less adequately describe the reaction. The catalytic reaction can be divided into the following steps:



The first step is the dissociative adsorption of nitrogen and hydrogen on the catalytic surface (Equations 2.2 and 2.3). The adsorbed nitrogen is then hydrogenized in the three reactions in Equations 2.4, 2.5, 2.6 until ammonia is formed. Ammonia will then desorb from the surface (Equation 2.7) [6].

Based on these steps, with appropriate assumptions, different models have been obtained. The first and most frequently adopted model is the Temkin and Pyzhev one. It was written in 1940, and it is still used a lot today due to its simplicity and good prevision of the rate. It is derived by assuming that nitrogen adsorption is the rate-determining step and that nitrogen is the most abundant species on the surface [7, 25, 26]. The Temkin and Pyzhev model is visible in Equation 2.8:

$$r = k_A p_{\text{N}_2} \left(\frac{(p_{\text{H}_2})^3}{(p_{\text{NH}_3})^2} \right)^\alpha - k_B \left(\frac{(p_{\text{NH}_3})^2}{(p_{\text{H}_2})^3} \right)^{(1-\alpha)} \quad (2.8)$$

Where:

p_i is the partial pressure of component i ,

k_A and k_B are the forward and backward rate constants,

α is a reaction constant, which expresses how the heat of absorption changes as a function of surface coverage [25, 26].

This equation does not consider transport limitation. An interesting and also largely used equation was proposed by Dyson and Simon. In their model (Equation 2.9), they rearrange the Temkin equation and introduce an effectiveness factor, η , which accounts for transport limitations, and can be determined either analytically or experimentally [27].

$$r = 2k[k_{\text{eq}}^2 p_{\text{N}_2} \left(\frac{(p_{\text{H}_2})^3}{(p_{\text{NH}_3})^2} \right)^\alpha - \left(\frac{(p_{\text{NH}_3})^2}{(p_{\text{H}_2})^3} \right)^{(1-\alpha)}] \eta \quad (2.9)$$

When not assuming nitrogen as the most abundant species, the kinetic expression assumes a more complex form, as proposed by Ozaki et al. [26] :

$$r = \frac{k_A p_{N_2} - k_B (p_{NH_3})^2 / (p_{H_2})^3}{[1 + k_C (p_{NH_3}) / (p_{H_2})^\gamma]^{2\alpha}} \quad (2.10)$$

Being the ammonia synthesis and high-pressure reaction, the non-ideality of the gas system should be considered. This has been done in the Nielsen et al. model, in which the partial pressures of the gases are substituted by their activities [25, 26]:

$$r = \frac{k_A a_{N_2} - k_B (a_{NH_3})^2 / (a_{H_2})^3}{[1 + k_C (a_{NH_3}) / a_{H_2}^\gamma]^{2\alpha}} \quad (2.11)$$

Process Design for Green Ammonia Synthesis

As explained in the previous paragraphs, the main features of the Haber Bosch process are the presence of a recycle, the use of a catalyst, and the high pressure in the reactor.

To recycle the unreacted gas, this needs to be separated from the product (i.e. ammonia). This is achieved by decreasing the temperature of the gas and using a separator. The respective disposition of the separator and reactor varies depending on the specific design. If the makeup gas contains catalyst poisons, the separator will be before the reactor, to allow for pollutant removal. This design strategy is based on the solubility of most of the possible pollutants (such as CO_2 and CH_4) is higher in ammonia than in the synthesis gas.

When, on the contrary, the makeup gas is practically pure, the separator will be positioned after the reactor, being the most cost-efficient solution. Namely, it allows for more efficient separation, as it happens where the ammonia percentage in the gas is higher. Moreover, this option reduces the flow rate to the recirculating compressor [6, 7].

When considering green ammonia production, both the hydrogen and nitrogen can be assumed to be at very high purity, therefore the second option is more adequate. Moreover, being the synthesis gas so pure, the purge is not needed in normal operations. It is however usually added for safety reasons [28]. A schematic representation of the overall design is reported in Figure 2.3. The gas is compressed to the synthesis required pressure before entering the loop. Then it is mixed with the recycle stream. Here another compressor is needed, which presents a very low compression factor as its main requirement is to circulate the gas in the loop and recover from the pressure drop experienced by the gas in the rest of the equipment. In the schematic representation, the heat exchangers are

not reported. However, it is interesting to point out that one of the first features of the ammonia synthesis plant is the feed effluent heat exchanger. This heat exchanger is positioned before the reactor, and it employs the reactor product to heat the reactor feed [6].

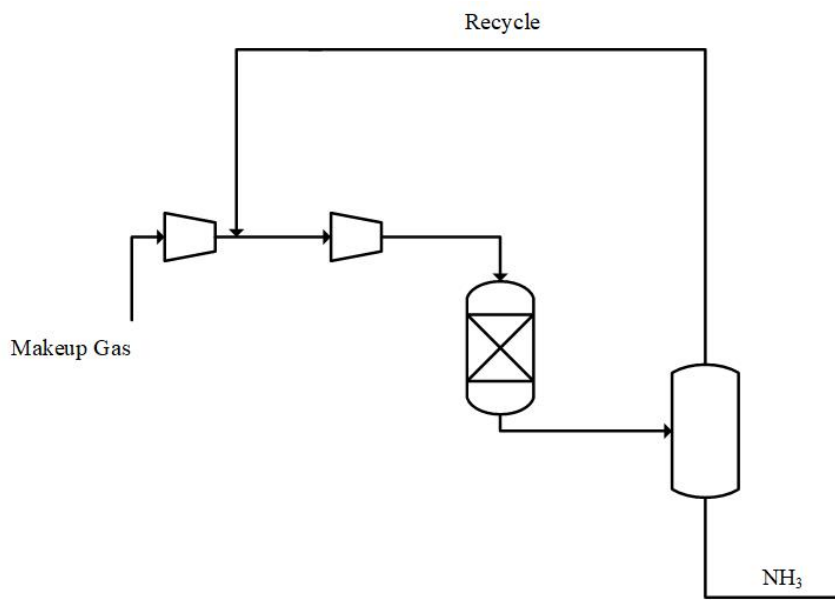


Figure 2.3: Simple process flow diagram of ammonia synthesis loop.

Reactor design. Through the years, different configurations for the ammonia synthesis reactor have been developed to increase the reactor efficiency. This means, producing the higher amount of ammonia with the lower amount of catalyst. To do that, the conditions in the reactor need to be as close as possible to the maximum rate line, which is the locus of temperatures and conversions at which the rate is maximum. It is important to underline that this differs from the equilibrium line, as the latter is at higher values of temperature (and conversions) [6].

To achieve this, the gas in the reactor needs to be cooled down. The reactor is therefore divided into multiple catalytic beds, and the temperature is decreased between the beds. There are two main options to do that: quenching or indirect cooling, which are shown in Figure 2.4.

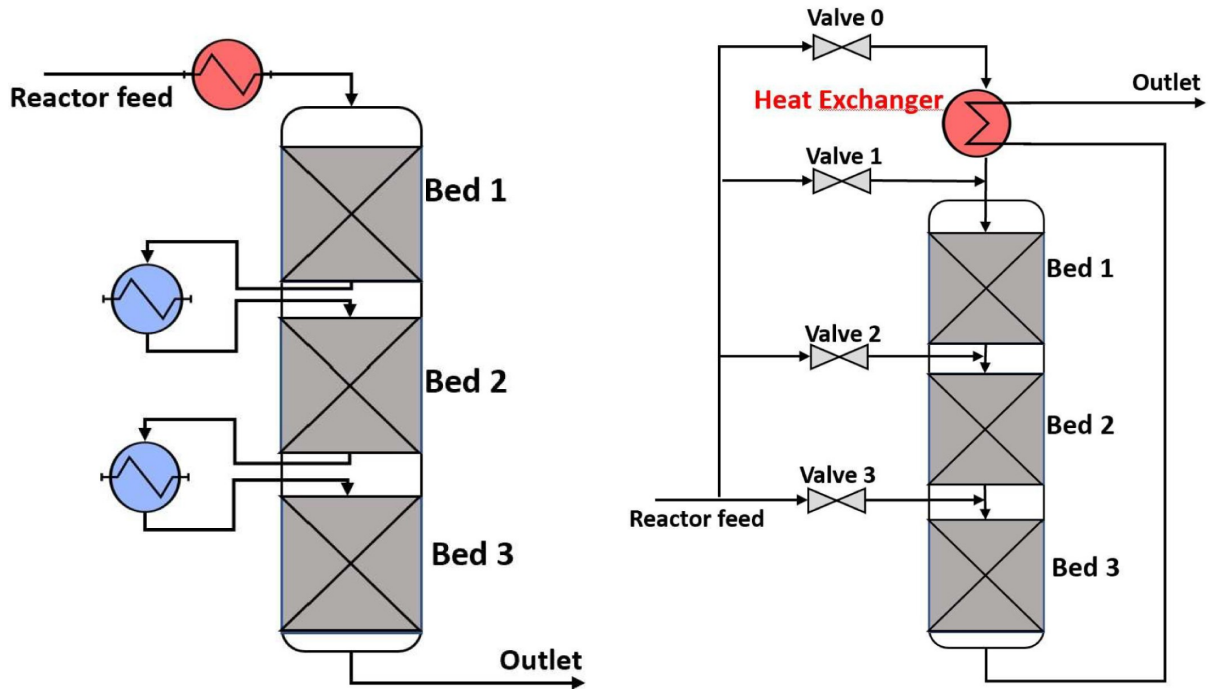


Figure 2.4: Structure of an indirect cooling reactor for ammonia synthesis, on the left, and a quench cooled reactor, on the right [29].

With indirect cooling, on the left in Figure 2.4, heat exchangers are added to the reactor to decrease the fluid temperature. In this case, high-pressure steam can be generated or the feed is used as a cooling medium [6]. With quenching, on the right, part of the feed is inserted at different reactor lengths, to decrease both the temperature and the ammonia concentration. The two different designs are correlated with two different operating lines. The one with intercooling is reported in Figure 2.5, and the one with quench cooling is reported in Figure 2.6. In both cases, the gas increases temperature and ammonia concentration in the catalytic beds. If intercooling is used, the temperature between the catalytic beds is reduced but the ammonia concentration is maintained. If quenching is used, both the temperature and ammonia concentration are reduced after each catalytic bed, as the quench with the synthesis gas decreases the ammonia percentage in the flow (diagonal dashed lines).

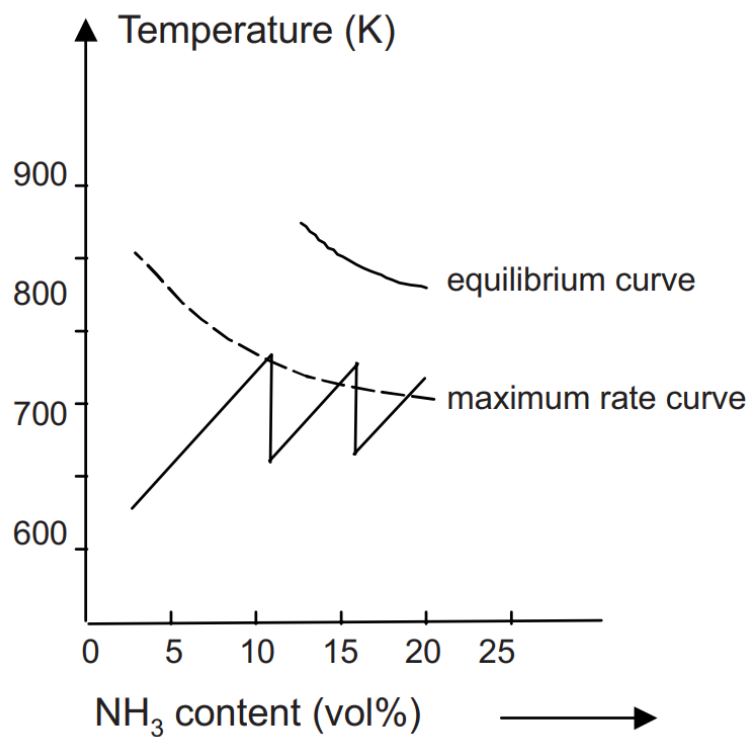


Figure 2.5: Operating line for an ammonia synthesis in a multibed converter with indirect cooling [6].

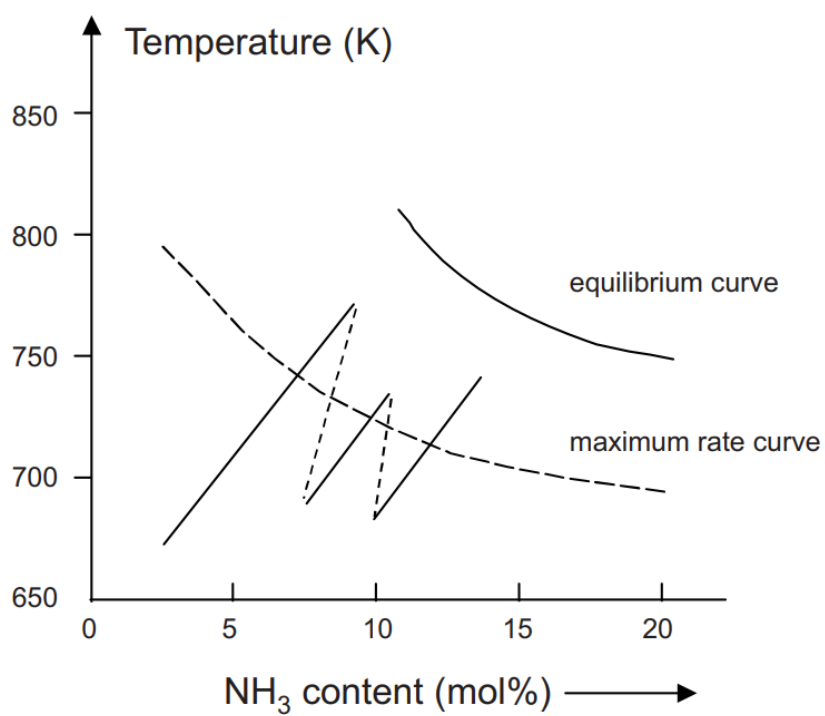


Figure 2.6: Operating line for an ammonia synthesis in a quench reactor [6].

Looking specifically at green ammonia synthesis and operation at different loads, there are studies in the literature that aim at optimizing the reactor design to increase its flexibility. For instance, Fahr et al. [30], optimize the design of an ammonia converter to allow for better partial load operations. The reactor in this case is a three catalytic beds reactor with feed effluent heat exchanger and intercooling, in which the feed serves as cooling medium.

2.2. Steady State Simulations and Results

To carry out a dynamic simulation it is fundamental to first have a steady-state study. The system, as described in section 2.1, was simulated at a steady state in a previous work [11]. In this section, a summary of the assumptions considered and results obtained is provided. The image of the simulation can be found in Appendix A.2.

2.2.1. Assumptions Considered in the Steady State Simulations

The project consisted of the studying of how the reduction in the make-up gas load would affect the synthesis loop conditions. With this aim, the plant was simulated at different loads, with the 100% load corresponding to 10000 kg/h of Ammonia produced, which will be referred to as nominal capacity. The equipment was sized accordingly. The reactor considered is a three-bed catalytic bed reactor with intercooling in which the cooling medium is the feed, as observable in Figure 2.7, and the pressure drop in each catalytic bed has been evaluated with the Ergun equation, available in UniSim design.

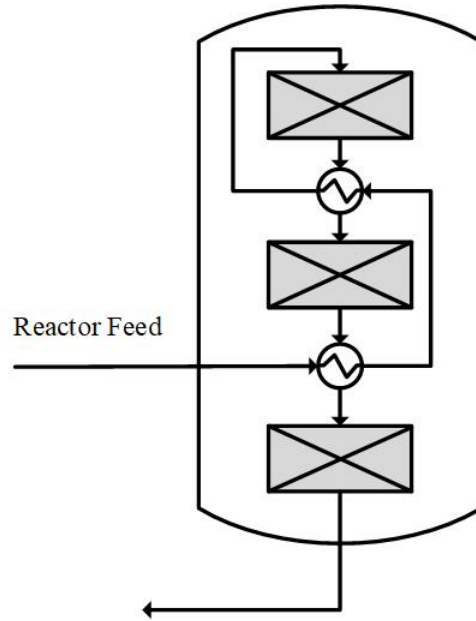


Figure 2.7: Schematized representation of synthesis reactor for steady-state analysis.

The main challenge was found in modeling the heat exchangers. The question that had to be answered was how the pressure drop and the heat transfer coefficient change when the flow rate in the heat exchanger is reduced. The pressure drop in the heat exchangers was considered as 50 kPa at full load, and reduced accordingly with the volumetric flow reduction, according to Equation 2.12 :

$$\Delta P_1 = \Delta P_0 \frac{\dot{V}_1^2}{\dot{V}_0^2} \quad (2.12)$$

Understanding how the heat transfer coefficient would change was more complex. When designing the process at full load, the desired temperatures are fixed, and the heat exchanger is designed accordingly. For instance, for a desired temperature change ΔT , the required duty, Q , is calculated as:

$$Q = \dot{m}cp\Delta T \quad (2.13)$$

Where:

Q = Required duty

$\dot{m}$ = Mass flow rate

cp = Specific heat

ΔT = desired temperature difference

Then the area required is obtained:

$$A = \frac{Q}{U \Delta T_{ml}} \quad (2.14)$$

Where:

A = Heat exchange area

U = Heat transfer coefficient

ΔT_{ml} = Mean logarithmic temperature

From the required heat transfer area, the heat exchanger can be sized in detail, i.e., for a shell and tube heat exchanger, the number and size of the tubes, the shell size, the number of tube and shell passes, etc, can be defined.

But what happens when in a specific heat exchanger the flow rate is reduced? Will the temperature be affected?

Two options have been considered to answer these questions:

- Considering the heat transfer coefficient (U) constant when reducing the flow rate
- Considering the heat transfer coefficient (U) proportional to the flow rate

The obtained results are reported in the next paragraph. The second option is a simplification obtained from the heat exchanger design procedure in [31]. Namely, when conducting a design procedure, the heat transfer coefficient, at each side of the heat exchanger, is calculated as proportional to the Nusselt number, which is proportional to the velocity elevated by 0.8 ($v^{0.8}$) when the flow is turbulent, and to the velocity elevated by 0.33 ($v^{0.33}$) when it is laminar [31].

2.2.2. Results Obtained from the Steady State Simulations

The result depended mainly on the assumptions considered for the heat exchangers. As explicative of the first option, when the heat transfer coefficient is considered constant, the temperature variations in the first catalytic bed are reported in Figure 2.8. In this figure, the independent variable is the load percentage (% of Base Case Flow Rate), which is reducing from left to right. The base case, at 100% load, corresponds to an ammonia production rate of 10000 kg/h. Therefore 20% of the base case flow rate will correspond to an ammonia production rate of 2000 kg/h. The blue line corresponds to no temperature

control in the system (case 1), while the red line corresponds to the results associated with the use of a cold shot stream to keep the temperature constant (case 2). In this case, it appears evident that temperature control is needed to maintain the temperature in the catalyst operating range.

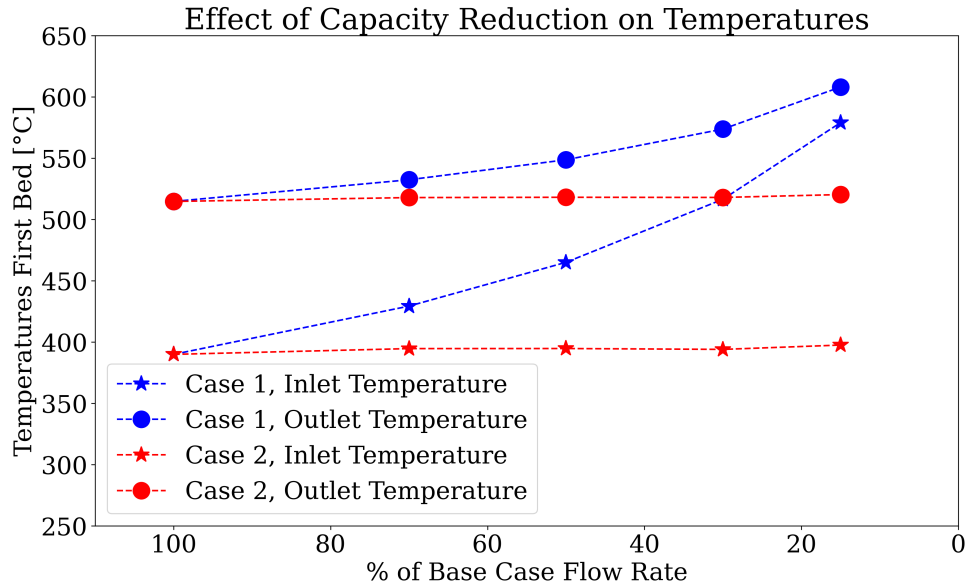


Figure 2.8: Steady State Temperatures in the first catalytic bed, UA constant [11]

The results related to when the transfer coefficient was supposed to be proportional to the flow rate are exemplified in Figure 2.9, which corresponds to case 3 of the project [11]. In this figure, the outlet temperature from the first, second, and third catalytic beds are reported as a function of the load percentage. It is possible to observe that, when the heat transfer coefficient is supposed to be proportional to the fluid velocity in the reactor, the temperatures in the system do not undergo any substantial change.

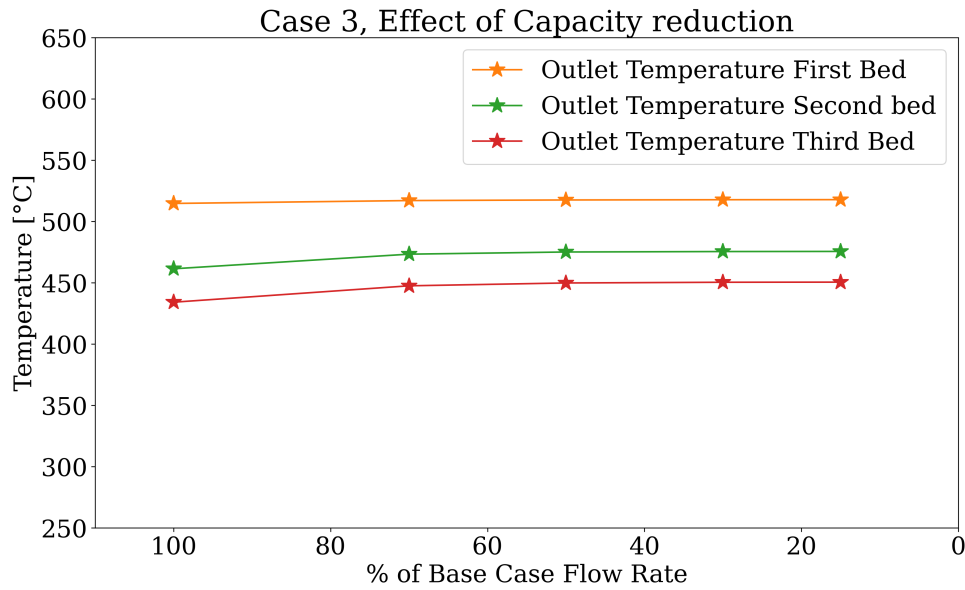


Figure 2.9: Steady State Temperatures in the reactor, UA adjusted [11]

As mentioned above, the heat transfer coefficient will probably not be proportional to the velocity nor remain constant. It is logical to assume that the reality should lie between the two cases: with a temperature increase in the first catalytic bed that will be less than what is depicted in Figure 2.8, but more than in Figure 2.9. With a dynamic simulation, it should be possible to reach more definitive conclusions.

2.3. Dynamic Simulations and Control Strategies for a Flexible Green Ammonia Plant

In this Section, an introduction to dynamic simulation and control is given. This is followed by specific control strategies for ammonia synthesis plants.

2.3.1. Introduction to Dynamic Simulation and Control

As previously explained, a steady-state simulation gives fundamental information about the studied process, but it does not allow for the study of time-dependent behaviors, which can be important for studying start-ups and shutdowns, unusual disturbances, and planned transitions [12]. This project aims to understand the behavior of an ammonia synthesis loop when the hydrogen makeup varies to accommodate renewable energy fluctuations. For this reason, a dynamic simulation will most definitively improve the process understanding.

In this section, some fundamentals on process dynamics and control are given.

The dynamic model consists of a set of equations that can describe the system, typically ordinary differential equations or partial differential equations. There exist different software packages that present dynamic features, such as Aspen + Dynamic, UniSim Dynamic, and DynSim. In software-aided dynamic simulation, the software solves the dynamic model and gives an output that is variable in time. The technique used to solve these equations is chosen as a compromise between computing time and accuracy of the results [12]. For instance, the method used in UniSim dynamic is the Implicit Euler method with fixed time steps. Implicit methods are often more stable than explicit methods, as they can handle also stiff problems, while having fixed time steps allows for lower computational times [32]. The dynamic solver uses pressure-flow equations to solve the system, To do that, equipment sizing is needed. It is not necessary to have a specific mechanical design but information about gas volume and liquid holdup is necessary for the solver to run the simulation [33]. Some equipment can be sized approximately by using the steady-state data directly through the dynamic simulator, for others, a different approach needs to be considered [33].

Process control is fundamental for the safe operation of a chemical plant. Moreover, it is needed to produce the desired product quantity and quality, abide by technical and operational constraints, satisfy environmental requirements, and increase economic performances [12, 34]. When considering green ammonia synthesis, process control gains the specific role of adapting the plant operation to hydrogen availability since a flexible synthesis has been proven to be beneficial [9, 35].

The effect that the controllers have on the process depends on their tuning. For instance, a controller can change a process variable faster or slower and can increase or decrease oscillating behaviors in the process. Different tuning techniques can be used. The SIMC tuning technique for PID controllers is explained here since it is regarded to be simple and effective [36], and it has been used in some examples for ammonia synthesis [37, 38].

The term PID stands for 'proportional, integral, derivate'. The action of this controller is divided into three different parts: proportional, integral, and derivate. Equation 2.15 is the proportional part of the PID controller.

$$u = u_0 + K_C(y_S - y) \quad (2.15)$$

In this equation, the response is proportional to the error. The error is $(y_S - y)$, where y is the process variable, and y_S is the desired setpoint. $u - u_0$ is the change given by the

controller. k_C is the first tuning parameter. If this equation is implemented, the controller is a P-controller.

Equation 2.16 also includes the integral part of the controller.

$$u = u_0 + K_C(y_S - y) + k_C \frac{\int_0^t e(t)dt}{\tau_I} \quad (2.16)$$

In this equation, the integral of the error ($e(t) = y_S - y$) is considered. τ_i is the tuning parameter, called 'integral time'. When this equation is used, the controller is a PI controller, which is the most used in the industry.

The complete equation for a PID controller is:

$$u = u_0 + K_C(y_S - y) + K_C \frac{\int_0^t e(t)dt}{\tau_I} + K_C \tau_D \frac{de(t)}{dt} \quad (2.17)$$

In this case, also the derivate of the error is considered, and it is multiplied for the third tuning parameter, τ_D [12].

The first step in using the SIMC rule is to study the step response of a process, which means evaluating the open loop response to obtain the process gain (k), process time constant (τ), and process time delay (θ).

Once these parameters have been obtained, the tuning parameters are calculated as follows:

$$k_C = \frac{1}{k} \frac{\tau}{\tau_C + \theta} \quad (2.18)$$

$$\tau_I = \min(\tau, 4(\tau_C + \theta)) \quad (2.19)$$

$$\tau_D = 0 \text{ or } \tau_D = \tau_2 \quad (2.20)$$

Where τ_C is the desired response time, τ_2 is the second order time constant. For tight control, τ_C can be selected equal to θ , while for loose control τ_C is to be selected bigger than θ [36].

2.3.2. Control Structure for Ammonia Synthesis

The study of a dynamic and flexible plant is relatively new as explained in the introduction. Nevertheless, there is a growing amount of specific studies on green ammonia and a large number of studies on conventional ammonia synthesis plants, which are significant in the understanding of the synthesis process and its control.

The effect of a sudden decrease in the makeup gas flow rate has been observed in an incident in an industrial Ammonia reactor in Germany in 1989 and studied by Morud and Skogestad, 1998 [39]. The sudden decrease in the flow rate led to an oscillating behavior of the temperature in the reactor, with a range of 200 °C, as observable in Figure 2.10.

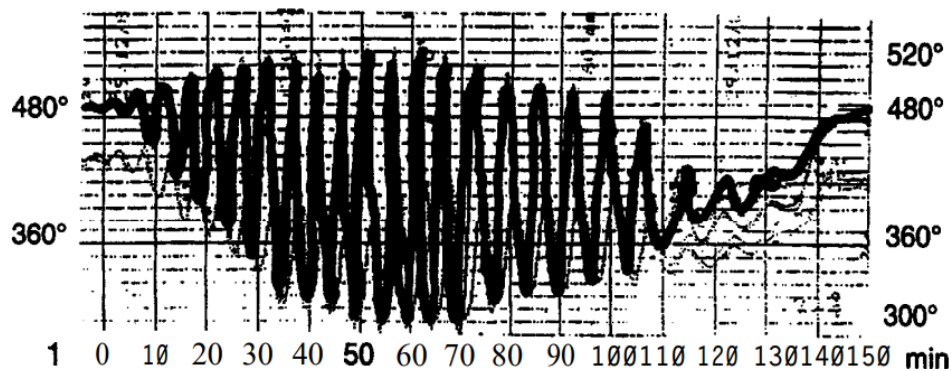


Figure 2.10: Instability recorded in an industrial ammonia reactor after a sudden decrease in makeup gas flow rate [39].

The authors modeled the reactor and explained the observed limit cycle behavior. The reactor considered in this case is a fixed bed reactor made of three catalytic beds in series with quench as the cooling method. In this configuration, part of the feed is heated in the feed effluent heat exchanger and then sent to the first catalytic bed. The remaining part is divided between the first, second, and third catalytic beds, and it has the function of cooling the feed to each of the beds. The authors modeled the reactor (without the preheater) with a dynamic model, where they were able to reproduce the oscillations observed in industry. They analyzed the results both with a steady state analysis and a linear dynamic analysis, as they argue that the steady state is insufficient to study the case. They discuss that if a significant decrease in pressure is observed, this could lead to a shutdown of the entire system and suggest stabilizing the system with a controller. They suggest introducing a quench valve to the first reactor so that the temperature of the first catalytic bed is kept stable even if the pressure in the system is subjected to

disturbances.

This article has been studied by Mancusi, Merola, and Crescitelli in 2000 [40]. These authors consider the dynamic model proposed by Morud and Skogestad and conduct a complete dynamic analysis of the system, arriving at similar conclusions.

Morud and Skogestad's model has also been used by García et al. [37], to propose a three-level control strategy, which can be seen in Figure 2.11 [37]. The first level has the main focus on stabilization, the second provides the temperature set point for the first level, introducing a cascade controller, which was also suggested by Morud and Skogestad in [39], and finally, a third level, which is aimed to optimize the ammonia production. The first level is achieved by three PI controllers which adjust the quench flow rate at each of the three catalytic beds, the second level is used to stabilize the system in a larger operative range. To do that, a cascade control to the temperature of the first reactor is implemented. The cascade control considers the outlet temperature from the reactor and changes consequently the set point to the temperature controller in the first bed. This solution had been proposed to stabilize the reactor temperature and allow lower operating conditions in 1981 by Giles and Gaines [41]. The third level considers the optimization needed to maximize ammonia production, which goes beyond the scope of this project. The implementation of an overall control structure aimed at improving process performance is well explained in [42], and has been used to implement a control structure for ammonia synthesis by Araújo and Skogestad, 2008 [38]. In these papers, the controllers have been tuned following the SIMC rule reported in [36].

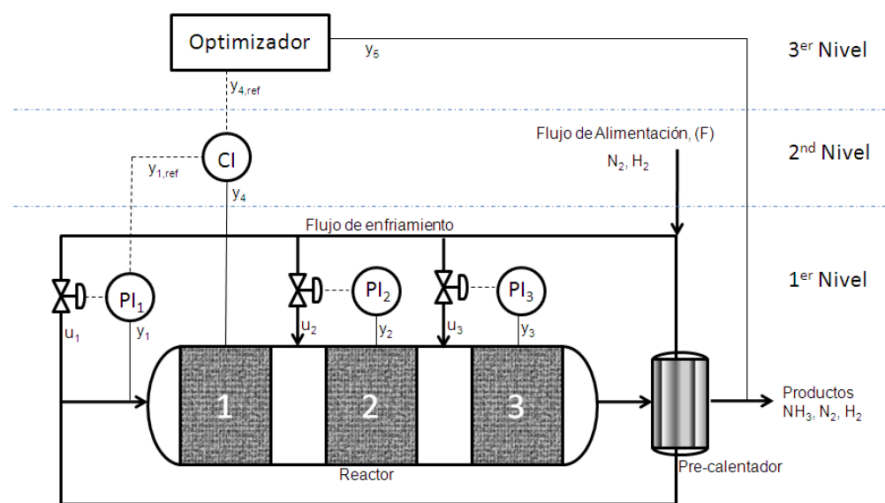


Figure 2.11: Three level control strategy for ammonia synthesis [37].

With green ammonia, the challenge of stable operation in the reactor has increased in complexity, as the system needs to be able to adapt to lower flow rates of hydrogen in the feed. Considering that green ammonia could be one of the most important actors in the carbon neutrality goals, it is a predictable consequence that different articles can be found on dynamic simulation and control of ammonia synthesis [1, 2, 35, 43–47].

Verleysen et al., 2022 [45], propose a design with three catalytic beds, a feed-effluent heat exchanger, and a second heat exchanger between the second and third catalytic bed, as seen in Figure 2.12. In this configuration, the feed is split: part is used as cold fluid in the two heat exchangers, and part as a quench before the second catalytic bed. These flow rates are controlled through valves, which, they argue, allow for temperature control to the first and second catalytic beds, and the flow inlet at the second catalytic bed. Their strategy consists of keeping the temperatures in the beds to the optimal operating value.

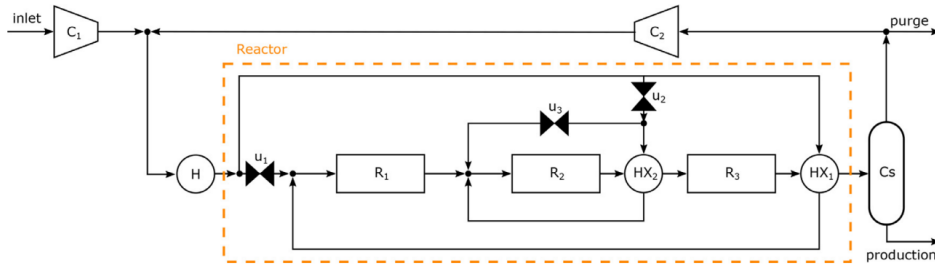


Figure 2.12: Reactor design of a flexible green ammonia plant according to [45].

Koschwitz et al. focus on a design in which they propose to heat the feed with an electrical pre-heater instead of a gas-gas heat exchanger, to increase the operating flexibility [35]. The reactor considered in this case is three catalytic beds with quench. They simulate the system in Aspen Plus Dynamic, demonstrating its applicability. The control strategy involves controlling the temperature at each catalytic bed, by combining electrical heating and air cooling. The pressure in the reactor is controlled by the purge valve and the recycle valve. The recycle valve is the first that is adjusted, while the purge is used only if necessary. They state that the recycle valve allows them to avoid the need for a double compressor in the recycle stream, hence decreasing greatly the capital investment.

Rosbo et al, 2023 [46], developed a dynamic model for ammonia synthesis with a control structure able to stabilize the system in an operating range of 0.2 to 1.2 the nominal capacity. With nominal capacity, they intend the designed plant capacity. The reactor they consider is a three catalytic bed reactor with quench and feed effluent heat exchanger, as Morud and Skogestad [39] and others [37, 38, 40]. The parameters for modeling the reactor in this article are also taken by Morud and Skogestad [39]. They consider a

cascade control for the reactor temperature, in which they use as a control variable (CV) the inlet temperature to the first bed, as seen in [37, 39]. Based on the inlet flow rate and the outlet temperature from the reactor, they calculate the optimal temperature at the reactor inlet, and this is given as a set point in the feedforward control, which adjusts the cold shot. They do not mention the pressure control in the reactor.

The most straightforward method for pressure control would be to adjust the speed (and therefore the duty) of the recirculating compressor. This method has been considered for conventional ammonia plants in [48] and it is one of the suggested methods for pressure control in systems with recycle [49]. However, some may argue this method is not economically advantageous in the case of ammonia production as it requires the makeup gas compressor and the recirculating one to be on different drivers, increasing the capital cost [2, 30].

Casale SA [2] and Haldor Topsøe A/S [1] both have patented a different synthesis loop which, they state, is suitable for operation in which green hydrogen is used. The design they propose should be able to operate at loads down to 10 or 20% of the design load. They commonly patent the possibility of using the anti-surge valve of the recirculating compressor as a pressure control valve. They state that having a constant ratio between make-up gas and converter feed gas will ensure constant pressure and temperatures in the reactor, avoiding oscillations. The anti-surge valve can be used for this purpose as the actions are never contradictory and the compressor protection will have, in any case, priority [1]. This solution is visible in Figure 2.13.

– Use of recirculator antisurge valve as loop pressure control valve

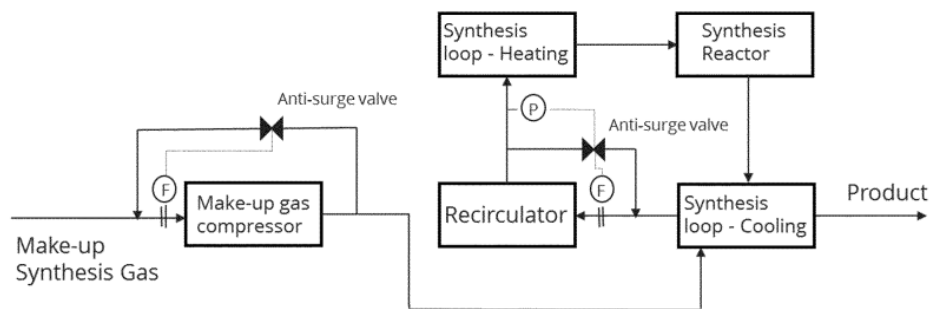


Figure 2.13: First design patented solution by Topsøe [1].

However, Topsøe patented different layouts for this purpose, visible in figures 2.14, 2.15 and 2.16 [1]. In the second option, Figure 2.14, it is assumed that the anti-surge valve can not be used as a flow control valve. Therefore, the stream is split and two valves

are introduced. The anti-surge valve has the fastest control, and it is usually closed. The pressure is controlled by recirculating a high amount of gas around the compressor, preventing it from going to the reactor. In this way, they argue, the amount of gas can be kept constant, maintaining the pressure into the desired ranges. The third option, Figure 2.15, differs in how the streams and valves are positioned. The purpose of this configuration is to allow for even lower loads in the system. This configuration is similar to the pressure control proposed by Koschwitz et al. [35]. In both cases the pressure in the system is increased by closing a valve along the synthesis loop: this will decrease the flow rate to the reactor. The fourth configuration also considers the addition of a ratio controller at the inlet, for the nitrogen-to-hydrogen ratio in the makeup gas. The other options consider that this ratio is practically constant. However, the said fluctuation could slightly affect the said ratio and therefore influence the nitrogen-to-hydrogen ratio at the reactor feed. For this reason, two real-time analyzers are added both at the makeup gas and reactor feed [1].

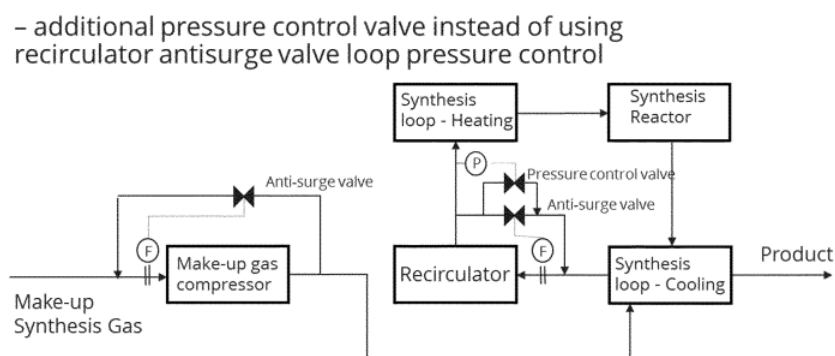


Figure 2.14: Second design patented solution by Topsøe [1].

– Use of additional valve(s) as loop pressure control valve

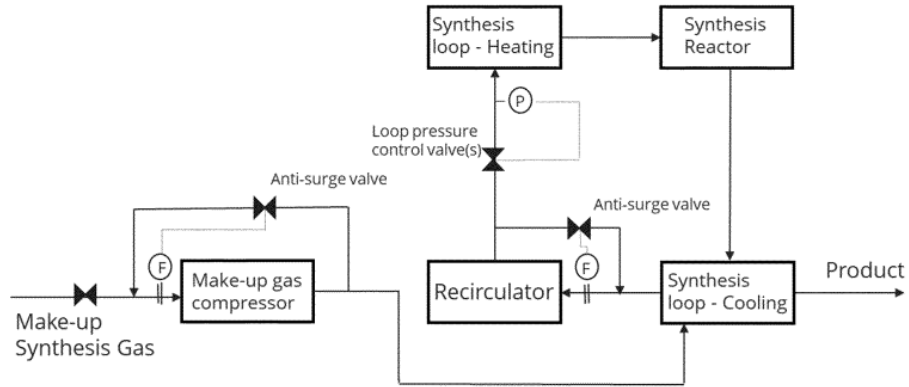


Figure 2.15: Third design patented solution by Topsøe [1].

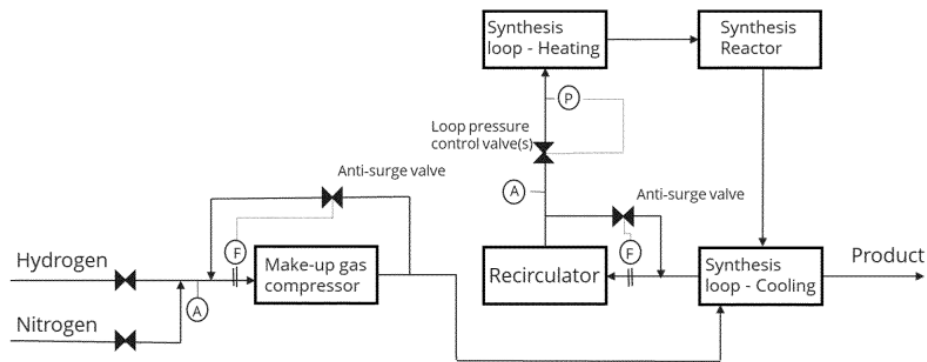


Figure 2.16: Fourth design patented solution by Topsøe [1].

2.3.3. Other Controls

Apart from the temperature and pressure in the reaction system, other controllers, called 'an surge controllers' need to be implemented. The surging is a highly unwanted phenomenon that can occur in a compressor when the flow rate in the inlet to the compressor is reduced. As the scope of this project is to study the dynamic behavior of the synthesis loop when the makeup gas flow is reduced, it has been considered particularly important to implement anti-surge strategies in this simulation. To explain the surging, some basics on the centrifugal compressor operation need to be given. The centrifugal compressor's operative range can be described by characteristic curves. A characteristic curve is the locus of points of flow rate and pressure increase that a compressor can give when fixing the rotating speed [50]. An example of an operating curve at a fixed speed can be observed in Figure 2.17. The optimal operating point for the compressor is between points E and

B in the figure, where a decrease in flow rate corresponds to an increase in the delivered pressure ratio. Point B is characterized by maximum pressure ratio and maximum efficiency. If the flow rate is decreased at less than point B, the pressure ratio decreases with the decreasing flow. In this region, the phenomenon of surge can happen. When surging happens, a sudden drop in the delivery pressure is observed, coupled with a violent aerodynamic pulsation that will ruin the compressor [50]. For this reason, surge needs to be avoided. One way to do this is to install an antisurge control, which will detect when the compressor is operating next to the surge line and will send a signal to either increase the flow rate or change the rotating speed. However, the surge line, which is the locus of points after which surging happens, is difficult to predict, and no general means are there to do so [50]. Often it is considered as a surge limit curve the locus of points of maximum compression ratio (point B), and the surge controllers operate by considering this line as operating limit [51].

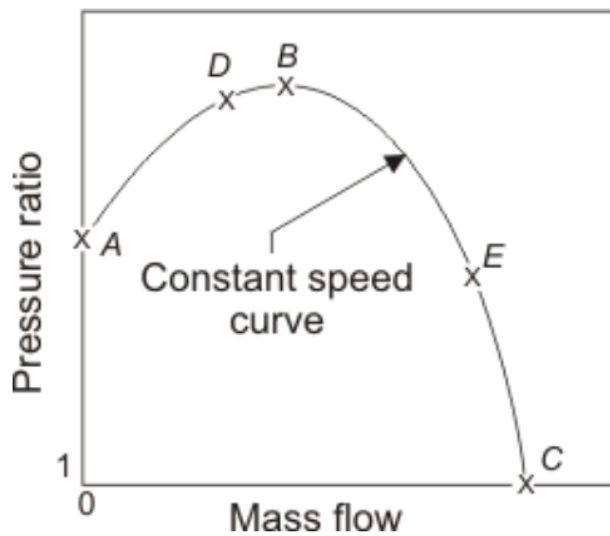


Figure 2.17: Theoretical characteristic curve [50].

3 | Design and Simulation

This chapter explains the methodology employed to complete the dynamic simulation of the green ammonia synthesis plant. Firstly, an overview of the chosen process flow diagram, without any control structure, is provided in Section 3.1. Section 3.2 explains how the dynamic simulation was conducted and the associated assumptions. The considered control structures are explained in Section 3.3. The image of the simulation is reported in Appendix B.

3.1. Process Flow Diagram

The process flow diagram (PFD) shown in Figure 3.1 schematizes the chosen design for the ammonia synthesis plant. The makeup gas, consisting of pure hydrogen and nitrogen (99.9%), undergoes mixing and is subsequently compressed in a two-stage compression train composed of two compressors: K-101 and K-102, and two heat exchangers: HX-101 and HX-102. The heat exchangers are needed to decrease the temperature, which increases with the compression, to around 25/30 °C.

The makeup gas is then blended with the recycle stream in another mixer and subsequently directed to compressor K-103. This compressor is needed to circulate the gas in the loop.

Following the compression, the gas enters the feed-effluent heat exchanger (HX-103), where it is heated to approximately 200°C using the exiting mixture of ammonia, nitrogen, and hydrogen from the reactor, which carries significant heat due to the high exothermicity of the reaction. Subsequently, the heated gas enters the reactor, which comprises three catalytic beds. The optimal temperature at the inlet of each bed is around 400 °C. Therefore, before entering the first catalytic bed the feed requires heating, accomplished through HX-104 and HX-105. In the first catalytic bed, the synthesis reaction starts to happen, which causes a temperature increase to about 520 °C. Subsequently, the gas requires cooling, which happens in HX-104. Here, the outlet gas from the first catalytic bed, at the elevated temperature of 520°C, acts as the hot fluid and is cooled down to around 400°C, while the feed gas serves as the cold fluid. Similarly, the gas exiting the

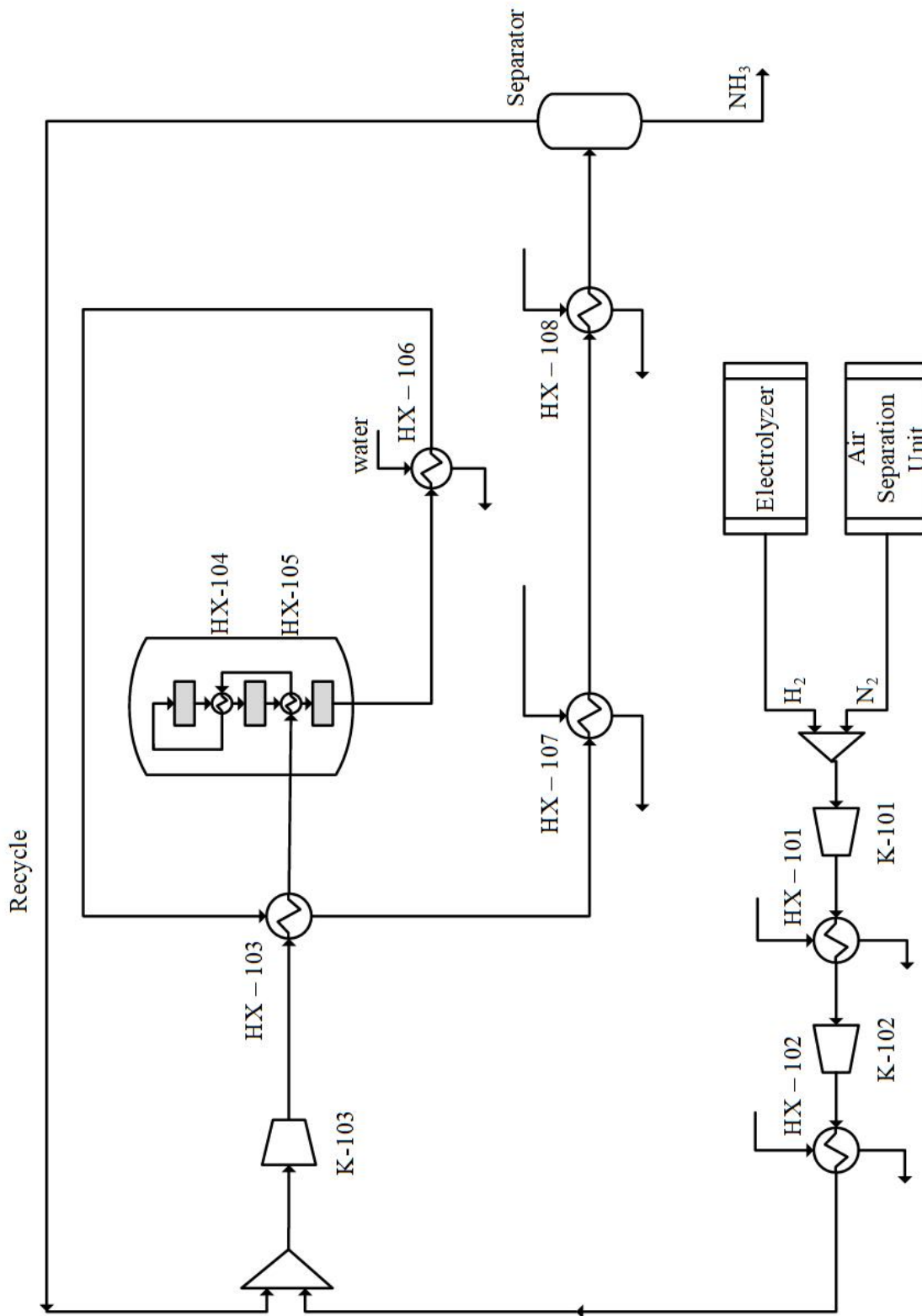


Figure 3.1: Ammonia synthesis loop implemented in the simulation.

second catalytic bed is cooled through the heat exchange with the feed stream in HX-105.

Following the third catalytic bed, a portion of the available heat is utilized in a waste heat boiler, represented simplistically as a waste heat heater, HX-106 (see Section 3.2 for details). The gas then proceeds to the feed effluent heat exchanger, serving as the hot fluid. Afterward, it undergoes cooling in HX-107 and HX-108. Once cooled, the ammonia can be separated from the unreacted gas, which is recycled. The loop does not feature a purge stream since the makeup gas is so pure that it is not needed [28, 30].

When conducting simulations of the entire system, identifying the equipment responsible for a specific phenomenon can be challenging. Therefore, the reactor with the waste heat boiler and feed effluent heat exchanger, as schematized in Figure 3.2 is studied separately before the comprehensive simulation. This simulation will be called 'partial simulation'. This approach allows for an understanding of how changes in load impact kinetics and temperatures within the reactor alone. The findings related to the partial simulation are detailed in Section 4.2 as they contribute significantly to a comprehensive understanding of the system.

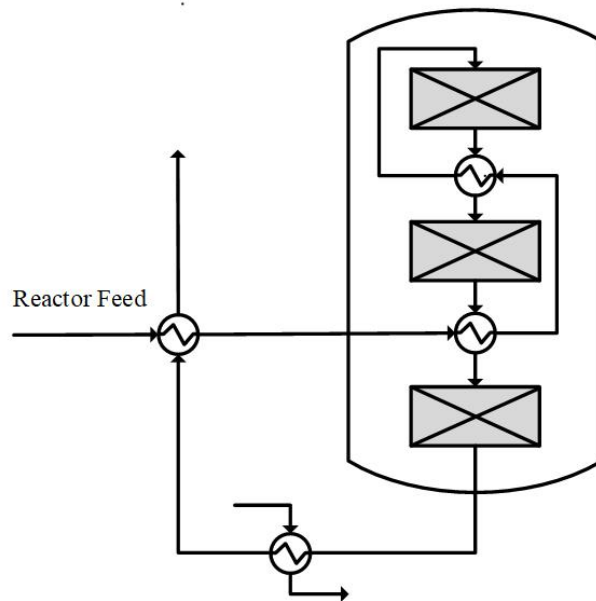


Figure 3.2: Process flow diagram implemented in the partial simulation, which includes the reactor with Feed effluent heat exchanger and waste heat boiler.

3.2. Dynamic Simulation of each Equipment

This section explains how the dynamic simulation of the plant was built. Figure B.1 reports the image of the overall simulation. Firstly, the most general assumptions on

the overall simulation are explained. Secondly, the assumptions made for each piece of equipment are reported.

In dynamic simulation, as explained in 2.3, all equipment needs to be sized. In this project, the system at 100% load is sized for a production rate of 10000 kg/h.

In UniSim Design, the solver uses the implicit fixed step size Euler method. There are two main options for this solver, one is 'flow-driven' and the other is 'pressure-driven'. The latter is more realistic [33], and it is the one chosen for this project. Consequently, the pressure at the boundary streams is set. The inlet pressure of hydrogen and nitrogen is 30 bar, while the outlet pressure of ammonia is 100 bar [28]. The makeup gas is brought to the synthesis pressure, around 150 bar, through the makeup gas compression train. The outlet ammonia pressure is greatly decreased through the last valve, after the separator. This is similar to what happens in reality and gives the solver the possibility to work also when a large pressure drop occurs in the system. Namely, if the solver determines a pressure in the system lower than the outlet pressure of ammonia, a reverse flow would occur, which is incoherent with reality.

Valves

Valves are one of the most important features in dynamic simulation which are not present in steady-state ones. They are essential for the UniSim solver, as they are pressure-resistance pieces of equipment, namely which are correlated to a pressure drop. In dynamic simulation, each pressure node equipment needs to be followed by a pressure resistance one [52]. Moreover, they play a crucial role in control purposes. Valve sizing requires the choice between different valve equations.

In this case, the easiest one, which is the simple valve equation (Equation 3.1), is chosen.

$$Flow = cv\sqrt{\Delta P\rho} \quad (3.1)$$

Where:

cv = valve conductance,

ΔP = pressure drop along the valve,

ρ = density.

Consequently, sizing only necessitates specifying the conductance (cv). This parameter is automatically computed once the pressure drop across the valve and the opening are defined. A higher pressure drop expands the operability range but also increases valve cost. Therefore, valve sizing is a trade-off between cost and operability range [33]. At

this stage, the simulation is needed to understand if the design proposed is operational, therefore valves are sized to allow for more plant flexibility.

Heat Exchangers

In UniSim Dynamic, heat exchangers can be solved either with the 'simple' model or with the 'detailed' model. The simple one consists of defining the volume of both the shell side and tube side, while the detailed one consists of specifying the heat exchanger TEMA type, and its characteristics. For shell and tube heat exchangers these include the tubes' size, diameter, number, shell size, baffle cut, and others. With the simple model for UniSim Dynamic, the volume of the heat exchanger must be calculated and it needs to be coherent with the required duty. A simple way to do this is starting from the heat exchange area required, following this procedure [33]:

$$V_{tubes} = \frac{D}{4} A_{total} \quad (3.2)$$

where :

A_{total} = total heat transfer area required,

D = chosen tube diameter.

$$V_{shell} = V_{tubes} \quad (3.3)$$

However straightforward this procedure may seem, it necessitates knowledge of the heat transfer coefficient. While a good starting point for heat transfer coefficients can be found in [31], it typically provides a range of values rather than a precise number. Additionally, how the heat transfer coefficient fluctuates with changes in flow rate remains unanswered when employing the simple model.

Therefore, the detailed model has been adopted for simulation. Specifications such as tube length, diameter, baffle spacing, etc., have been determined based on the guidance values in [31], and adjusted to simulation requirements such as flow rates and required heat transfer.

Waste Heat Boiler and Cryogenic Cooler

When modeling the waste heat boiler and the cryogenic cooler a change of phase needs to be accounted for. When there is a phase change a fictitious drum is necessary to model the fluid accumulation [53, 54].

For the sake of simplicity, and considering that the waste heat boiler is not the focus of this work, it has been modeled as a waste heat heater, without any phase change: high-pressure water is heated.

The cryogenic cooler, on the other hand, is simulated with the aid of a fictitious drum, as shown in Figure 3.3. The gas is cooled in HX-108 and sent to the fictitious drum, here there are two exits, one of which is closed. The second contains the mixture of gas and liquid to be sent to the actual separator. In this solution, the condenser is practically simulated in two pieces of equipment: HX-108, a shell and tube heat exchanger, and the fictitious drum. It is important to underline that in reality, these two pieces of equipment are part of the same one.

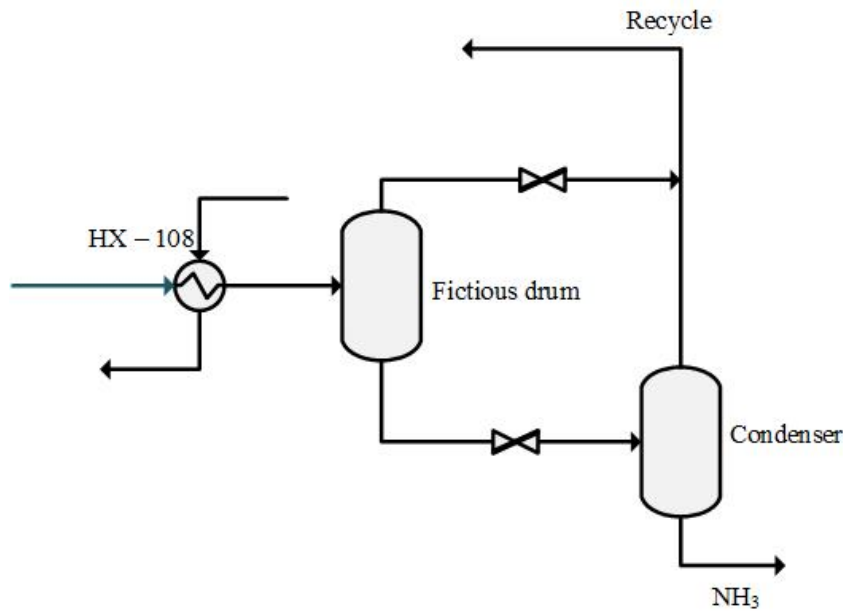


Figure 3.3: Cryogenic cooler and separator, simulation process flow diagram, with fictitious drum.

Compressors

For a compressor to be added to a dynamic simulation, two of the available dynamic specifications need to be chosen. These include duty, adiabatic or polytropic efficiency, head, speed, and use of characteristic curves. For this simulation, the use of characteristic curves has been chosen. This allows one to have more realistic results, especially when studying the phenomenon of surging (described in Section 2.3.3), as they allow for the implementation of an antisurge control (Section 3.3). The curves used are reported in Figures 3.4 and 3.5. These curves are taken from literature [55], they are, therefore, not specific to this project. The second parameter chosen is the compressor speed as it is the

one usually defined in reality [54, 56].

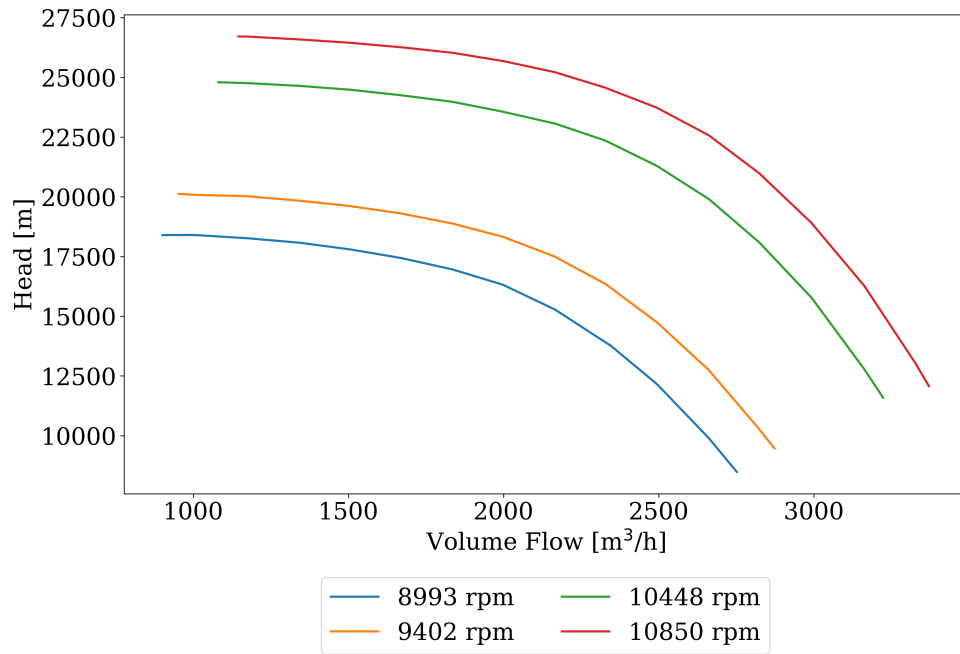


Figure 3.4: Curves employed in the simulation of the makeup gas compression trains, K101, K102 [55].

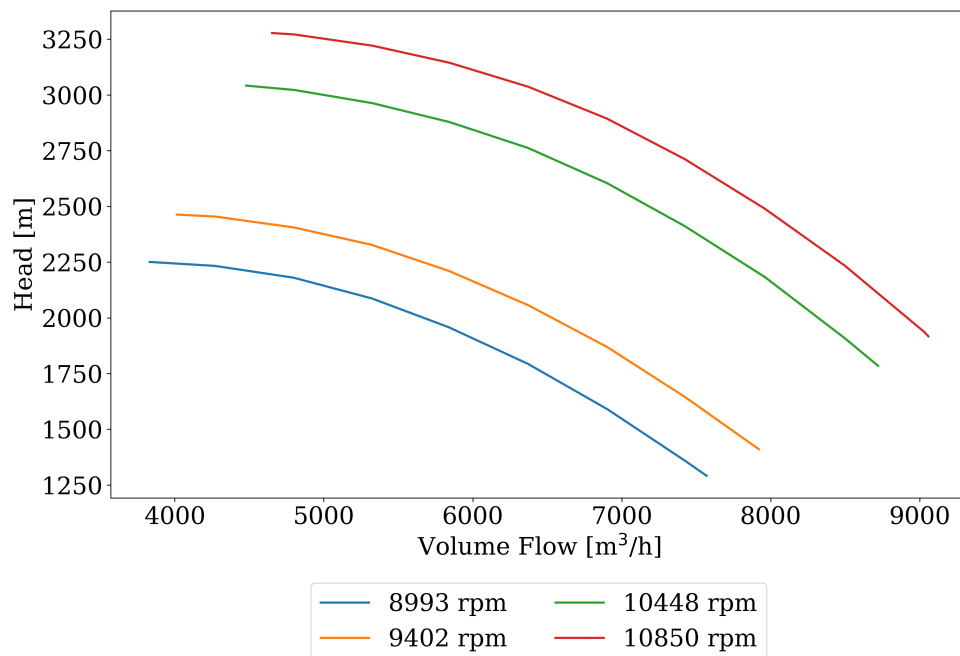


Figure 3.5: Curves employed in the simulation of the recirculating compressor, K103 [55].

Reactor

A scheme of the reactor, as in [57], is reported in Figure 3.6. It is composed of three catalytic beds with intercooling. The feed (light green) is heated in two heat exchangers before entering the first catalytic bed, as previously explained. It is also possible to observe the cold-shot: part of the feed that is directly sent to the first catalytic bed, bypassing the heat exchangers. This flow can be used as a temperature control, as seen in Section 2.3.2.

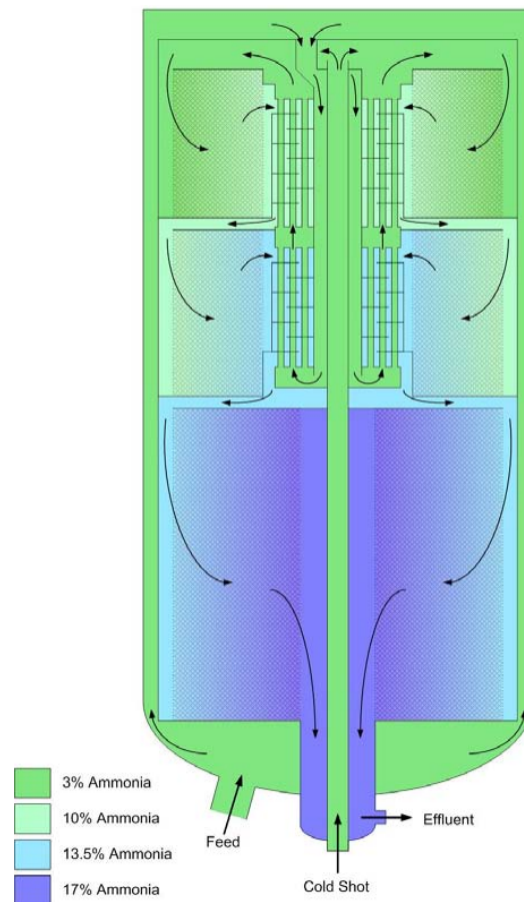


Figure 3.6: Topsoe S300 reactor scheme [57].

The reactor is modeled with three packed bed reactors and two heat exchangers. The heat exchangers have been modeled as previously explained. The sizing of the catalytic beds is done by using the sizing in [57], and assuming the volume is proportional to the plant capacity. The sizing parameters used are reported in Table 3.1.

Table 3.1: Sizing parameters used for the packed bed reactors.

Catalytic bed	Volume [m ³]	Lenght [m]
First	6.25	0.610
Second	6.25	0.641
Third	11.25	1.831

Table 3.2 summarises the parameters that are needed to simulate a PFR in UniSim Design. The void fraction has been chosen to be 0.45 which can be considered a typical value for packed bed reactors [58]. The particle diameter has been chosen considering the data reported in [59], while the solid density and solid heat capacity are those of iron oxide.

Table 3.2: Specifications used to simulate the packed bed reactors in UniSim Design.

Parameter	Value	Unit
Void fraction	0.45	-
Particle diameter	2.25	mm
Particle sphericity	1.00	-
Solid density	5170	kg/m ³
Solid heat capacity	0.45	kJ/kg °C

Kinetic Model

The three kinetic models explained in Section 2.1.2 have been previously analyzed. Some of the results of this analysis are reported in Appendix A.1. The most conservative approach would be to choose the Dyson and Simon kinetic model, as, considering the three catalytic beds, this gave the worst results in terms of conversion. This expression is, however, not possible to implement in UniSim. For this reason, the Nielsen et al. kinetic model is chosen. This model gives conversion values that are lower than the Temkin and Pyzhev model and it is sometimes regarded as more precise even if more complex [25–27]. For future considerations, it is useful to notice that the Nielsen model is faster than the other two at low conversion values, i.e., in the first catalytic bed. The model implemented in UniSim is here reported (Equation 3.4):

$$r = \frac{k_A a_{N_2} - k_B (a_{NH_3})^2 / (a_{H_2})^3}{[1 + k_C (a_{NH_3}) / a_{H_2}^\gamma]^{2\alpha}} \quad (3.4)$$

Where:

r is the reaction rate in kmol/m³/h,

a_i is the activity of species i in atm.

In table 3.3 it is possible to read the parameters used for this model, which are taken from literature [26, 60].

Table 3.3: Parameters for Nielsen Model rate expression, with r in kmol/m³/h, R in kJ/mol/k, T in K.

Parameter	Value
k_A	$3.289 \exp(+50.69/RT)$
k_B	$7.35 \cdot 10^{12} \exp(-59.04/RT)$
K_C	$0.0307 \exp(+81.0/RT)$
α	0.75
γ	1.5

Mixers and Splitters

Mixers and splitters can be specified in two primary ways: to ensure that the streams exiting the equipment match the pressure of the entering stream with the lower pressure, or to maintain uniform pressure across all streams, both entering and exiting the equipment. In this simulation, the second option is selected as it more accurately reflects real-world conditions [61].

3.3. Design of the Control Strategy

To develop a control structure it is important to understand which process variables need to be kept in a specific range. These have been chosen considering the literature review conducted in Section 2.3.2.

Firstly, various authors consider a flow control on the nitrogen and hydrogen flow rate at the beginning of the system [35, 46]. The hydrogen is adjusted based on its availability. The nitrogen flow rate controller, schematized in Figure 3.7 adjusts the nitrogen makeup gas flow rate to maintain a constant hydrogen-to-nitrogen ratio in the makeup gas when the hydrogen needs to be modified according to its availability. As described in Section

2.1, the hydrogen flow rate will depend on the renewable energy intensity, which varies considerably.

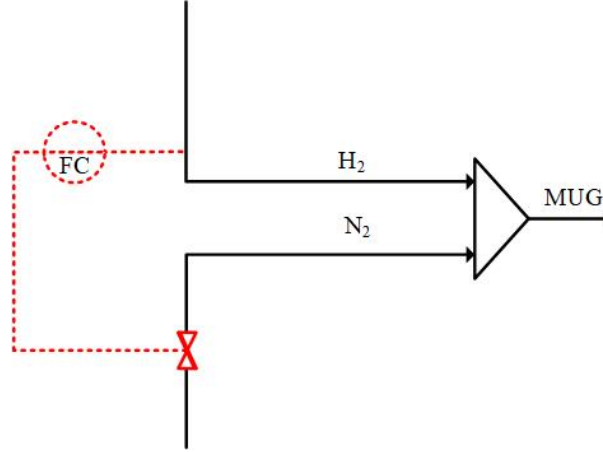


Figure 3.7: Flow control on nitrogen makeup.

When the flow rate is reduced, the compressors can experience the phenomenon of surging, as described in Section 2.3.3. For this reason, anti-surge controllers have been implemented. One anti-surge line has been implemented around the makeup gas compression train, and one around the recirculating compressor, as suggested in [1, 2]. The one around the compression train is schematized in Figure 3.8. To be implemented, the antisurge control needs the surge line. This is assumed to be the line that connects the operating point at the lowest flow rate for each of the characteristic curves in Figures 3.4 and 3.5.

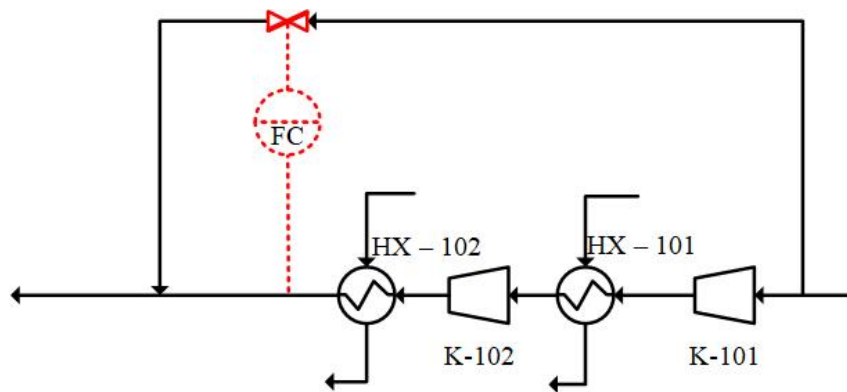


Figure 3.8: Anti surge control on makeup gas compression train.

Third, some authors consider the reactor temperature as a process variable that needs to be controlled [37, 39, 46]. According to these authors, a good option is to implement a control on the cold shot flow rate, which will adjust the cold shot flow rate to keep the inlet temperature to the first catalytic bed constant. Moreover, in some cases [45], the

implementation of a second temperature control, such as a quench valve before the second or third catalytic bed, is considered. In this case, as the quench option is not considered, bypassing the waste heat boiler has been considered. Both these control strategies are schematized in Figure 3.9.

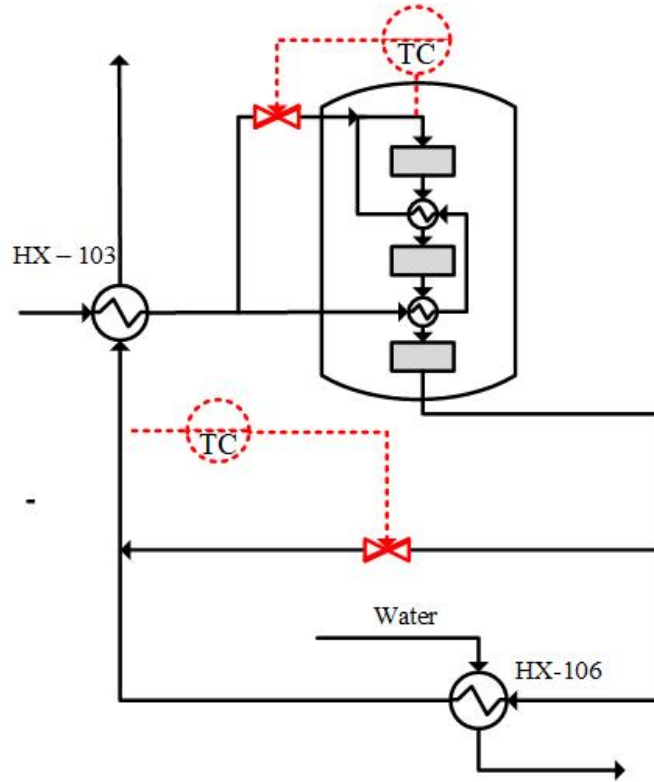


Figure 3.9: Reactor temperature control system.

Last, as seen in 2.3.2, when the flow rate is reduced particular attention should be given to the pressure in the system. Different pressure control strategies have been simulated in this work. First, the most direct way to control the pressure would be changing the compressor speed [48, 49]. This option, reported in Figure 3.10, has been simulated and the results are reported in Section 4.3.2.

According to [1, 2], the pressure can be kept constant by using the antisurge line around the recirculating compressor, or by adding a second line parallel to the antisurge one, as schematized in Figure 3.11. The choice between using a second antisurge line or one antisurge valve as both pressure and surge controller depends mainly on safety concerns. If there is the possibility that using the antisurge valve as pressure control could damage the valve or decrease in any way the process safety this should be avoided [1]. For this reason, using two antisurge lines around the compressor is the solution that could be most probably adopted in practice [28] and it is the one simulated in this work.

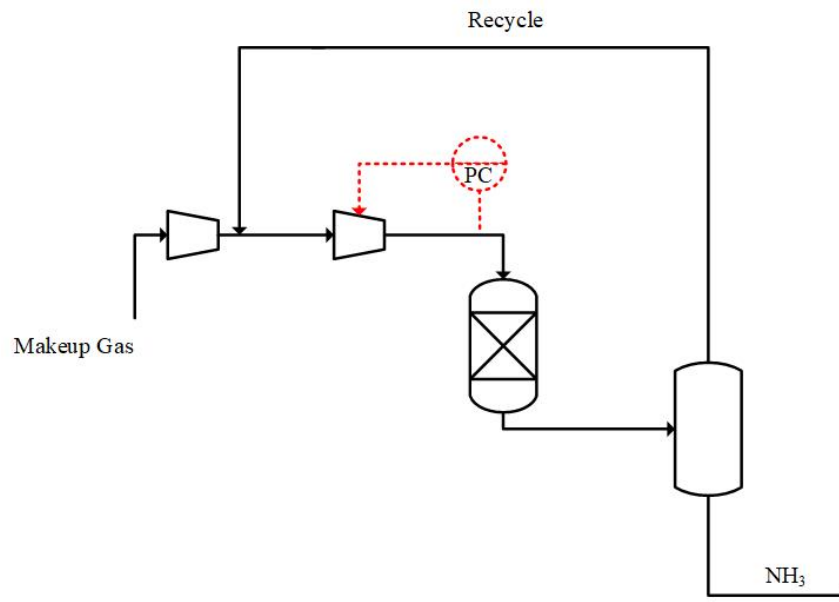


Figure 3.10: Scheme of pressure control which uses the compressor speed as manipulated variable. All the other controllers are omitted in the figure for clarity, even though they are in the simulation.

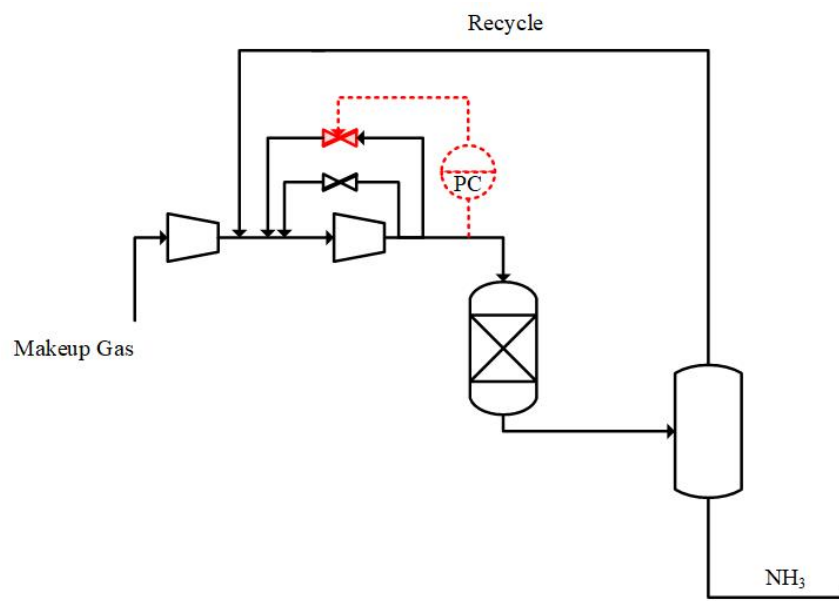


Figure 3.11: Scheme of pressure control which uses a second loop around the compressor as manipulated variable, all the other controllers are omitted in the figure for clarity, even though they are in the simulation.

According to [35], an important role in pressure control is given by the recycle valve, as in Figure 3.12.

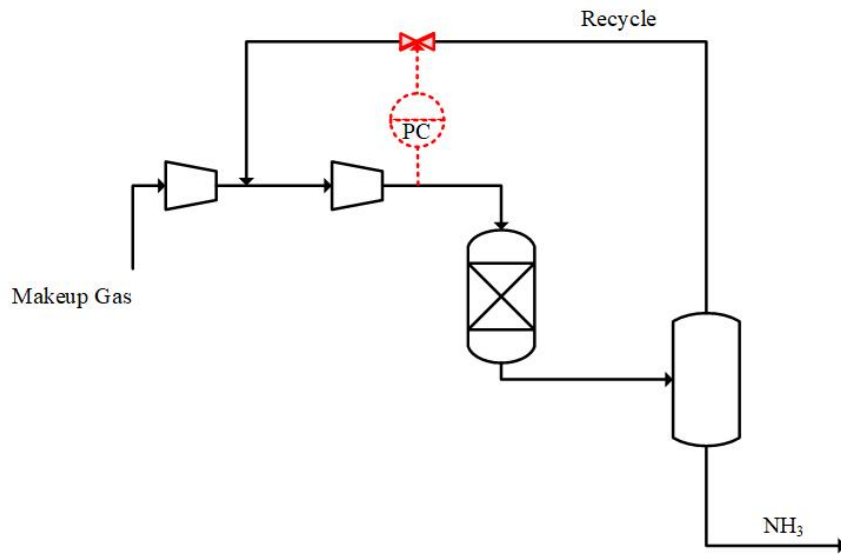


Figure 3.12: Scheme of pressure control which uses the recycle valve as manipulated variable, all the other controllers are omitted in the figure for clarity, even though they are in the simulation.

This option is very similar to one presented by Topsoe [1], which involves the use of a valve after the compressor, reported in Figure 3.13. These two options have been simulated and the results are reported in Section 4.3.4.

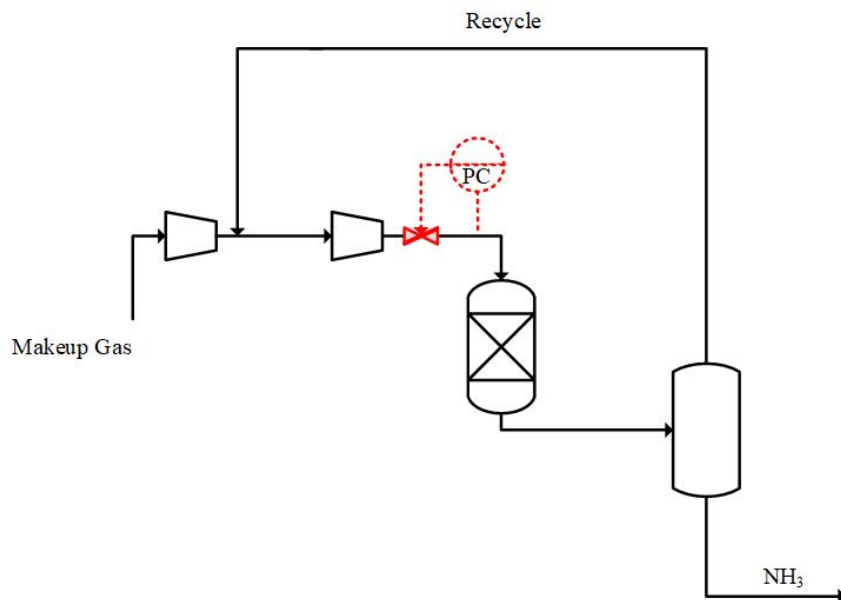


Figure 3.13: Scheme of pressure control which uses the valve after the compressor as manipulated variable, all the other controllers are omitted in the figure for clarity, even though they are in the simulation.

When conducting the simulation, it was observed that the temperature at the separator influences the rest of the plant. For this reason, the effect of a control system for this

temperature, as schematized in Figure 3.14 has been studied to understand if it is useful or necessary. Note that the level control has been kept for all the cases studied. This is because it is needed in the simulation to represent better the reality [58].

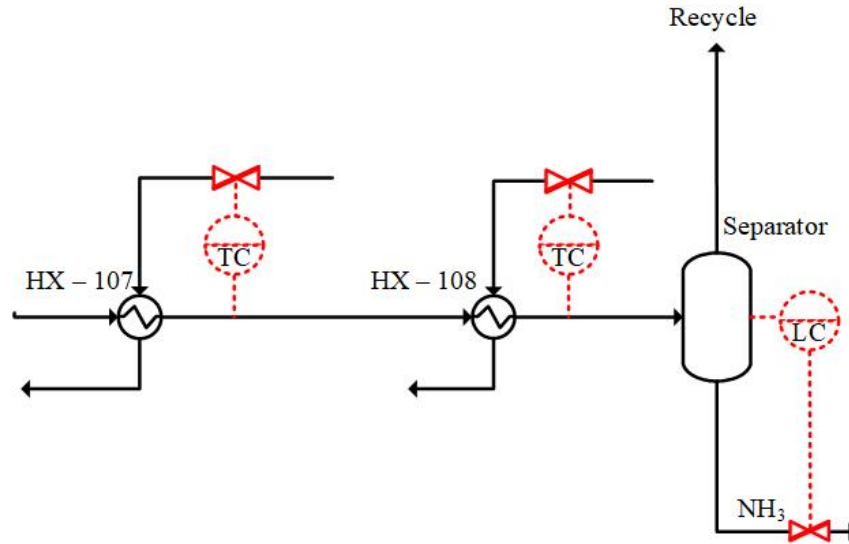


Figure 3.14: Possible temperature control structure on the separation section.

For all the controllers implemented, the parameters for the tuning have been calculated with the SIMC tuning method explained in Section 2.3 [36]. To obtain the needed parameters for the SIMC rule, i.e., the process time constant, the process gain, and the control delay, a step response has been studied for each controller. To do this, the manipulated valve opening has been changed instantly and the effect of this change on the process variable has been studied as suggested. The PI control in UnSim can be set either on direct or reverse action. It is reversed when the process gain is positive, which results in a positive K_C in Equation 2.17, and direct when the gain is negative, which results in a negative K_C in Equation 2.17 [32]. Therefore, when the obtained K_C is negative, the controller in UniSim needs to be set on 'direct'.

3.4. Limitations of the Model

There are different assumptions and simplifications that need to be considered when looking at the model results. First of all, however accurate the solver may be, it is still a model and as such can not predict perfectly reality. Moreover, looking more at the simulation assumptions, the compressors' characteristic curves are obtained from previous literature [55], and are not specific for this case study. The same goes for the kinetic parameters. The reactor model should also be discussed. It is a simplified model, in which

only one space direction is taken into account to solve the partial differential equations (the length). The waste heat boiler is modeled as a shell and tube heat exchanger, where the water is heated but no steam is produced. The cryogenic cooler, in reality, should see the cryogenic liquid evaporate [28], while in this simulation it is mostly liquid. Lastly, looking at the numerical method used by UniSim to solve the system, the implicit fixed-sized Euler method, this is a compromise between accuracy and speed [32]. When using a different solver, such as MATLAB, the accuracy will be fixed, and the system will iterate until the desired accuracy is met. This will improve accuracy at the expense of simulation time. In this case, the time step has been left to the default value of 20 seconds.

3.5. Scenarios Analyzed

In the context of green ammonia synthesis, the load variations will probably not be sudden but controlled with a ramp reduction, as these variations are part of the plant design and are not the result of an external disturbance. As discussed in section 2.1.1, daily energy fluctuations are to be expected when working with solar or wind power. For this reason, ramp reductions of three hours, from 100 to 20% have mainly been considered. Since some interest may be correlated to a reduction in a one-hour ramp, the results correlated to only one one-hour reduction are reported in Appendix D.1. To decrease the hydrogen makeup, a PI controller on the hydrogen flow rate is used. The setpoint of the controller is changed with a ramp from the initial value of hydrogen to 20% of the nominal value. This is carried out with the desired time interval of three hours. The scenarios analyzed are the following:

- Reduction of load from 100 to 80 % in one hour, without temperature or pressure control in the system, to understand the system's behavior.
- Reduction of load from 100 to 20% in three hours. Partial simulation which includes only the reactor, the waste heat boiler, and the feed effluent heat exchanger, to study and implement a temperature control structure on the reactor temperature.
- Reduction of load from 100 to 20% with different pressure control methods added to the previously defined temperature control. With this aim, the use of the compressor speed has been evaluated in Section 4.3.2, the possibility of using a second line parallel to the antisurge one has been analyzed in Section 4.3.3, the use of a valve along the synthesis loop has been analyzed in Section 4.3.4.
- Reduction from 100 to 50% in two hours, with or without the addition of a temperature control on the separation section.

In some cases (Section 4.2 and 4.3.3) a load increase is also analyzed. As this is reported to be mirroring the decreasing behavior, it has not been studied for all the cases.

4 | Results and discussion

This chapter explains and discusses the main results obtained. It begins with a simulation of a hydrogen load reduction to 80% without temperature or pressure control (Section 4.1). It then continues, in Section 4.2, with a focus on the reactor and the temperature control. This is achieved through a partial simulation, which includes the reactor, feed effluent heat exchanger (FEHE), and waste heat boiler (WHB), as shown in Figure 3.2. In Section 4.3 the effect of a load reduction on the system pressure is considered, and different control strategies, as reported in Section 3.3, are investigated. Finally, Section 4.4 examines how the separation temperature and its control can affect the system. The term 'load reduction' indicates the decrease in the hydrogen flow rate, which will result in the same decrease in the nitrogen makeup, given the flow controller. It is worth underlining that if the hydrogen flow rate is reduced and the conversion is kept around the same values, all the flow rates in the system will be reduced accordingly.

4.1. Reduction of Load Without Pressure or Temperature Control

The sudden reduction of load in the ammonia synthesis loop has been reported to cause a significant pressure decrease, possibly leading to limit cycle behavior when it drops excessively [39], instabilities have been recorded after the pressure is decreased from 200 to 170 bar. In this thesis, the focus is shifted to gradual reduction. The system's response to a load reduction from 100 to 80% load is examined in this paragraph. This reduction does not seem to lower the pressure to instability thresholds and it is useful to observe the system's behavior. The reduction is implemented in one hour. In Figure 4.1 some of the main results consequent to this reduction are reported. The hydrogen makeup is reported in subplot a, the pressure at the reactor inlet in subplot b, the conversions in the reactor in subplot c, and the temperatures in subplot d.

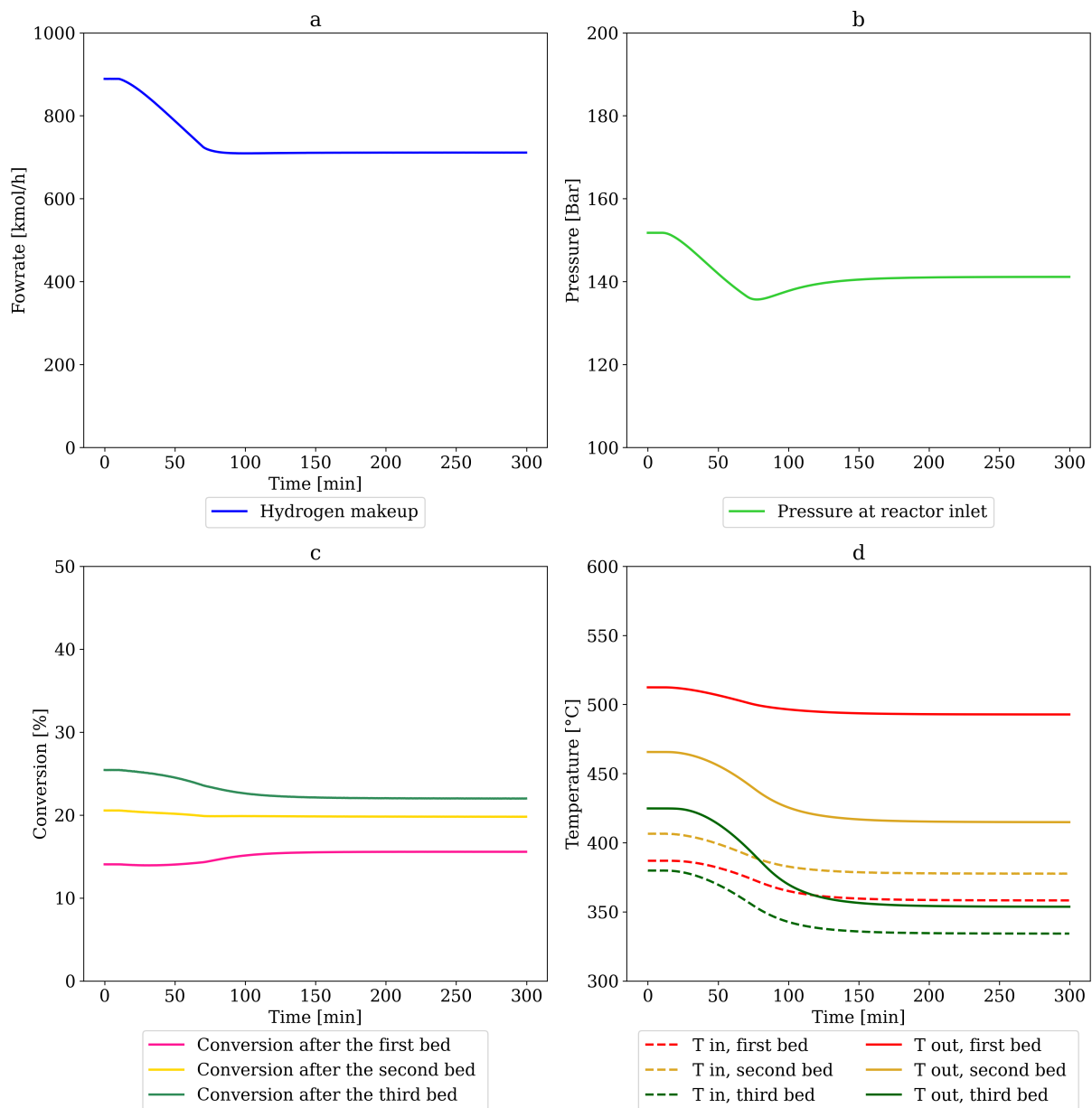


Figure 4.1: Results of a makeup hydrogen reduction from 100% load to 80% load in one hour, without any temperature or pressure control.

Looking at the pressure, it decreases from 152 bar to 141 bar. This is most likely due to the decrease in the amount of moles in the loop caused by the makeup gas load decrease. It is interesting to notice that the pressure reaches a minimum and then increases. This is probably due to the thermodynamics of the process. Namely, when the pressure is decreased, the conversion decreases (graph c), which, in turn, increases the recycle flow due to the stoichiometry of the reaction. The increase in the recycle flow will increase the pressure in the system. Observing Figure 4.1, it is possible to note that the reduction in pressure will decrease the conversion. This can be observed by examining the green

line in Figure 4.1 c. Since the reaction is exothermic, the reduction in the conversion will reduce the temperatures in the reactor, as observable in Figure 4.1 d. As the inlet and outlet temperatures of the catalytic beds are tied together by the intercoolers and FEHE, the reduction in the outlet temperatures will result in a reduction of the inlet ones as well. Moreover, the lack of control over steam generation results in more heat being used in this step than is optimal. The only conversion that is increased is the one in the first catalytic bed, as indicated by the magenta line in Graph c. In this case, the effect of decreasing the inlet temperature outweighs the effect of the decrease in pressure (high pressure and low temperatures favor the thermodynamics of the synthesis). It is important to note that this result could be exaggerated by the kinetic model used. This model, compared to others, gives higher rates for low conversion values. For more detail, refer to Appendix A.1. As seen in Section 2.1.2, the main concern regarding the temperature decrease is that, if the temperature reaches lower values than the minimum one of the catalyst operating range, where it is not active, the system will eventually shut down. Even if this does not happen, continued fluctuation of the pressure in the system will cause mechanical strain on the equipment, which will decrease its lifetime. For this reason, a control system that considers both the temperature and pressure in the reactor has been considered.

The effect of a load reduction on the reactor temperature range and relative control is studied in Section 4.2. The effect of the load reduction on the pressure and relative control strategies can be found in Section 4.3 while an analysis of how the separation temperature affects the system can be found in Section 4.4.

4.2. The Reactor and Temperature Control

In this section, the effect of a load change on the reactor temperatures is studied. With this aim, the simulation implemented is partial: it includes the reactor, the waste heat boiler, and the feed effluent heat exchanger, as schematized in Figure 3.2. The pressure in the system is defined at the system boundaries. Since these do not include the compressors, the separation, or the recycling of unreacted gas, the pressure is practically stable. While this simplification does not resemble reality, where all the mentioned above can affect the system pressure, it is considered beneficial to analyze the reactor behavior under stable pressure conditions.

In Figure 4.2 it is possible to observe the results of a decrease in load in the reactor when considering the partial simulation.

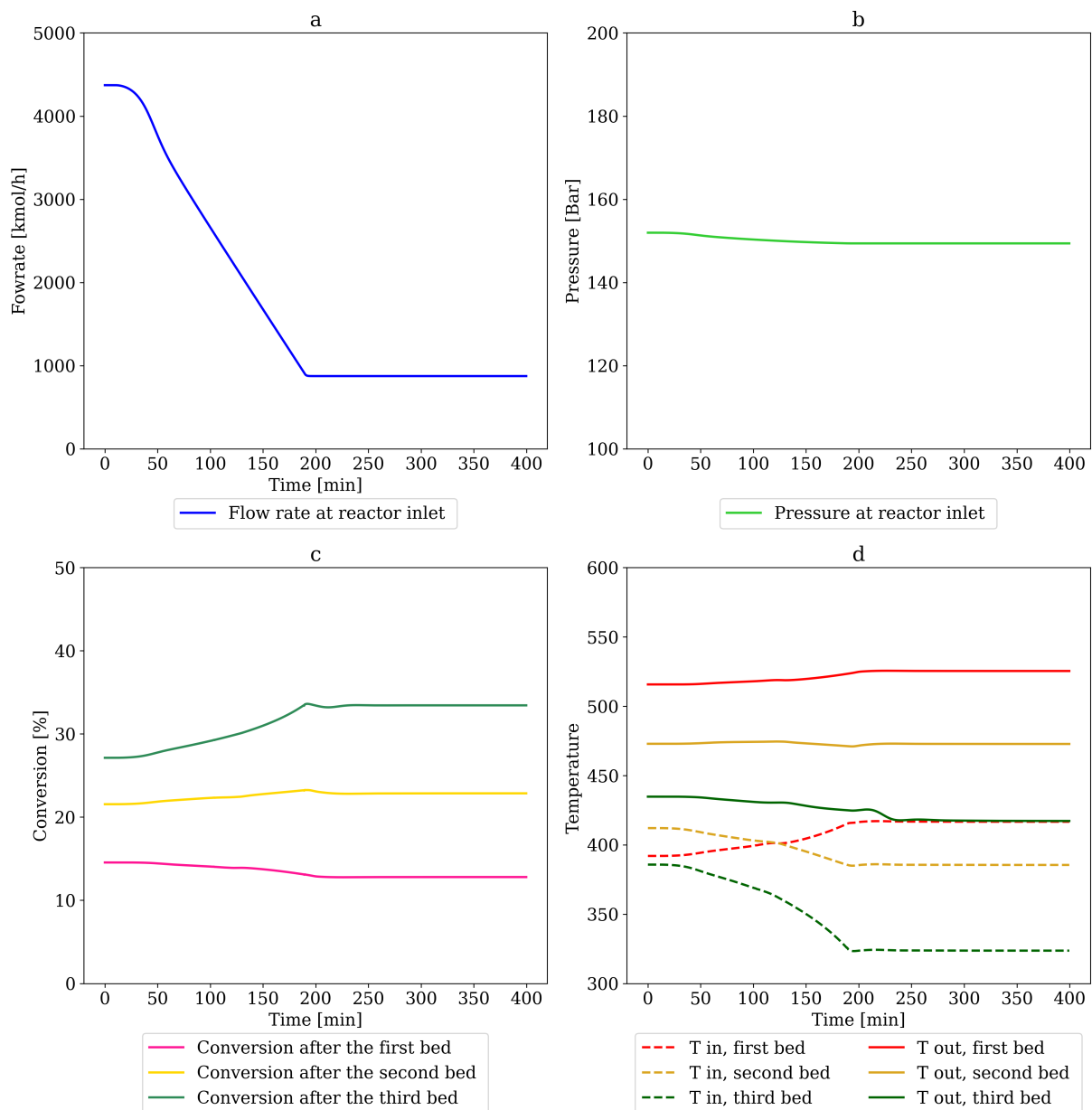


Figure 4.2: Partial simulation (reactor, feed effluent heat exchanger, and waste heat boiler). Results of a load reduction from 100 to 20% in three hours.

When decreasing the flow rate and keeping the other conditions constant, one could expect that the conversion will increase since the residence time is increased. This is indeed what it is possible to observe in Figure 4.2 c, the one pass conversion (green line) changes from 27% to 33%. For the same reason, the conversion in each bed should increase. This is, however, not the case in the first catalytic bed. To explain this, it is necessary to look at the temperatures in the reactor, reported in Figure 4.2 d. As it is possible to observe, the inlet temperature of the first catalytic bed increases when the load is reduced. This explains why the conversion in the first catalytic bed is reduced: since ammonia synthesis

is highly exothermic, an increase in temperature will disfavor the reaction. On the other hand, the inlet temperature to the third catalytic bed (green dashed line) decreases to 320°C. This temperature is outside the optimal operating range for the catalyst. This means that, in reality, the catalyst could be less efficient than what is simulated, possibly leading to system shutdown. Therefore, a temperature control may be needed. The reactor structure has been reported for clarity in Figure 4.3.

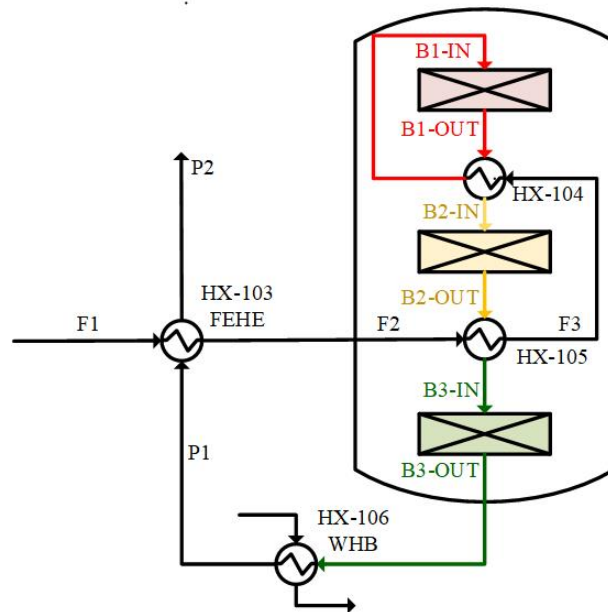


Figure 4.3: Reactor scheme.

The first thing to consider, as explained in Section 4.1, is that the WHB section is not controlled. When the flow is decreased, it is logical that also the steam produced should be decreased. When this is not done, the hot fluid in HX-103 (P1) will have less heat capacity than needed to heat the feed, which will, in turn, decrease the temperature of F2, and consequently, of B3-IN, as it has been observed in Figure 4.2 d.

The implementation of a WHB bypass is therefore considered, and the results are reported in Figure 4.4. As it is possible to observe, the inlet temperature of the third catalytic bed (green dashed line) is not as low as previously. However, when looking at the complete temperature range, it practically widens, with the maximum temperatures increasing and the lower ones decreasing. This is consistent with what is considered in Section 2.2. It was reported that the heat transfer coefficient at each side of the heat exchanger will be proportional to the velocity^{0.8} if the flow is turbulent. This would result in a reduction of the UA when the load is reduced, as reported in Figure 4.5, but not enough to keep the temperatures in the system constant. The heat exchangers

practically appear oversized, giving the observed result. This is also coherent with the procedure reported in Fahr et al. [30], as they consider the overall heat transfer coefficient proportional to a factor F , which is a function of the ratio between the actual molar flow and the designed one, elevated to 0.7.

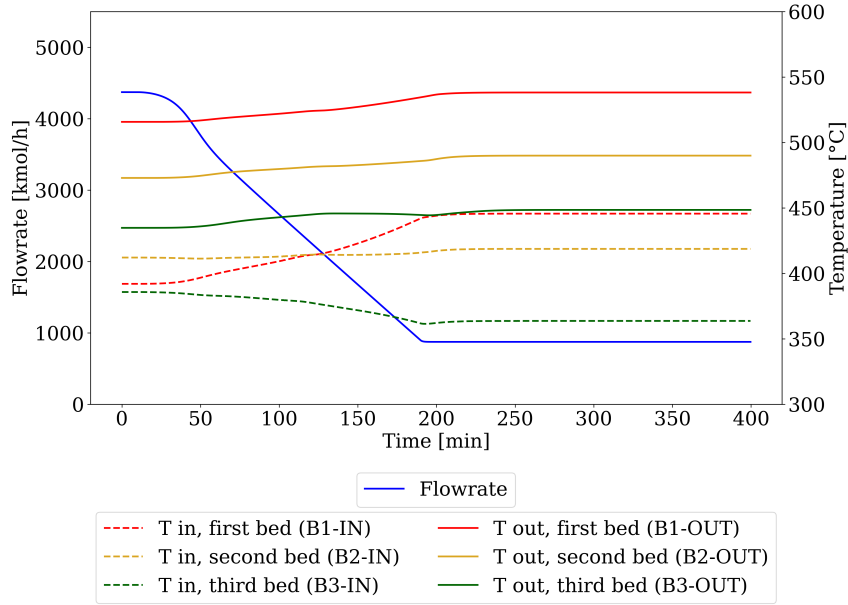


Figure 4.4: Temperatures in the reactor, partial simulation, when a control on the WHB is implemented, for a reduction of load from 100 to 20% in three hours.

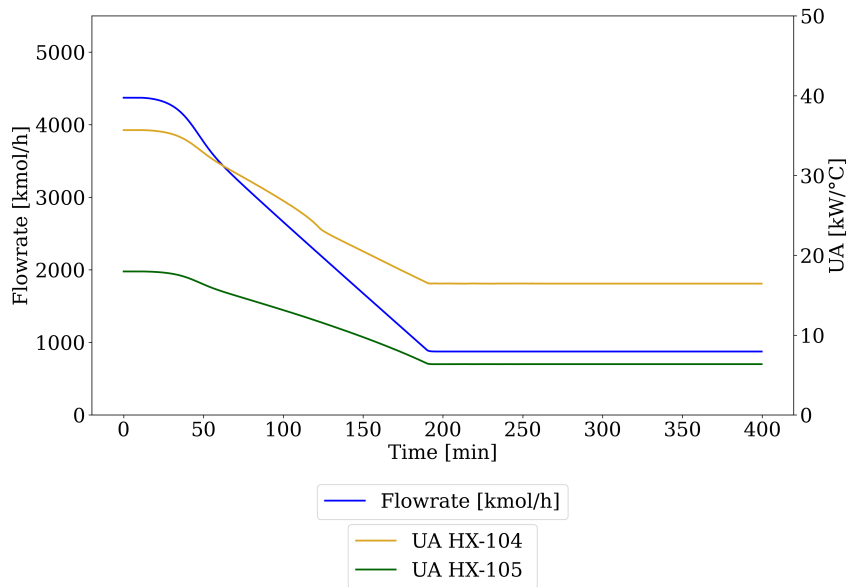


Figure 4.5: UA for the heat exchangers in the reactor, when the load is decreased from 100 to 20% in the partial simulation, and the control on the WHB is applied.

From a control perspective, it is important to notice that a high temperature in the reactor

can affect the catalyst's lifetime, and, for this reason, it usually needs to be avoided. The specific temperature range will depend on the specific catalyst formulation, which is not available at this point. If a lower maximum temperature is desired, the cold shot stream can be controlled to decrease the inlet temperature to the first catalytic bed.

The implementation of a cold shot stream is therefore evaluated, as suggested by [37, 39] (more details are available in Section 2.3.2). The temperatures in this case are reported in Figure 4.6. It is possible to observe that the temperature range is in the catalyst's optimal operating range. With this reactor configuration, two temperature controls are therefore suggested.

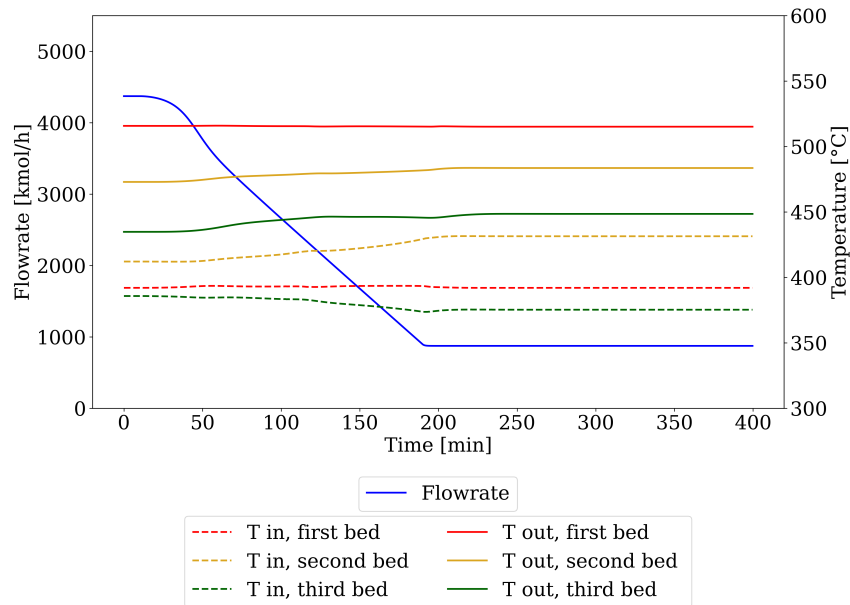


Figure 4.6: Temperatures in the reactor, partial simulation, when two temperature controls are implemented, for a reduction of load from 100 to 20% in three hours.

The overall results of a reduction from 100 to 20% are reported in Figure 4.7. It is interesting to also look at the conversion in the system, Figure c. It is possible to observe that in this case, the conversion in the first catalytic bed (red line) is practically constant, as the inlet temperature to the reactor is fixed. It is possible to observe an increase in the overall conversion (green line), which is mainly due to the third catalytic bed: the inlet temperature to this bed is lower and the residence time is higher. Both these factors will increase the conversion. The inlet temperature to the second catalytic bed increases at minute 200, which corresponds to a decrease in the conversion after this bed, coherently with the thermodynamics of the process.

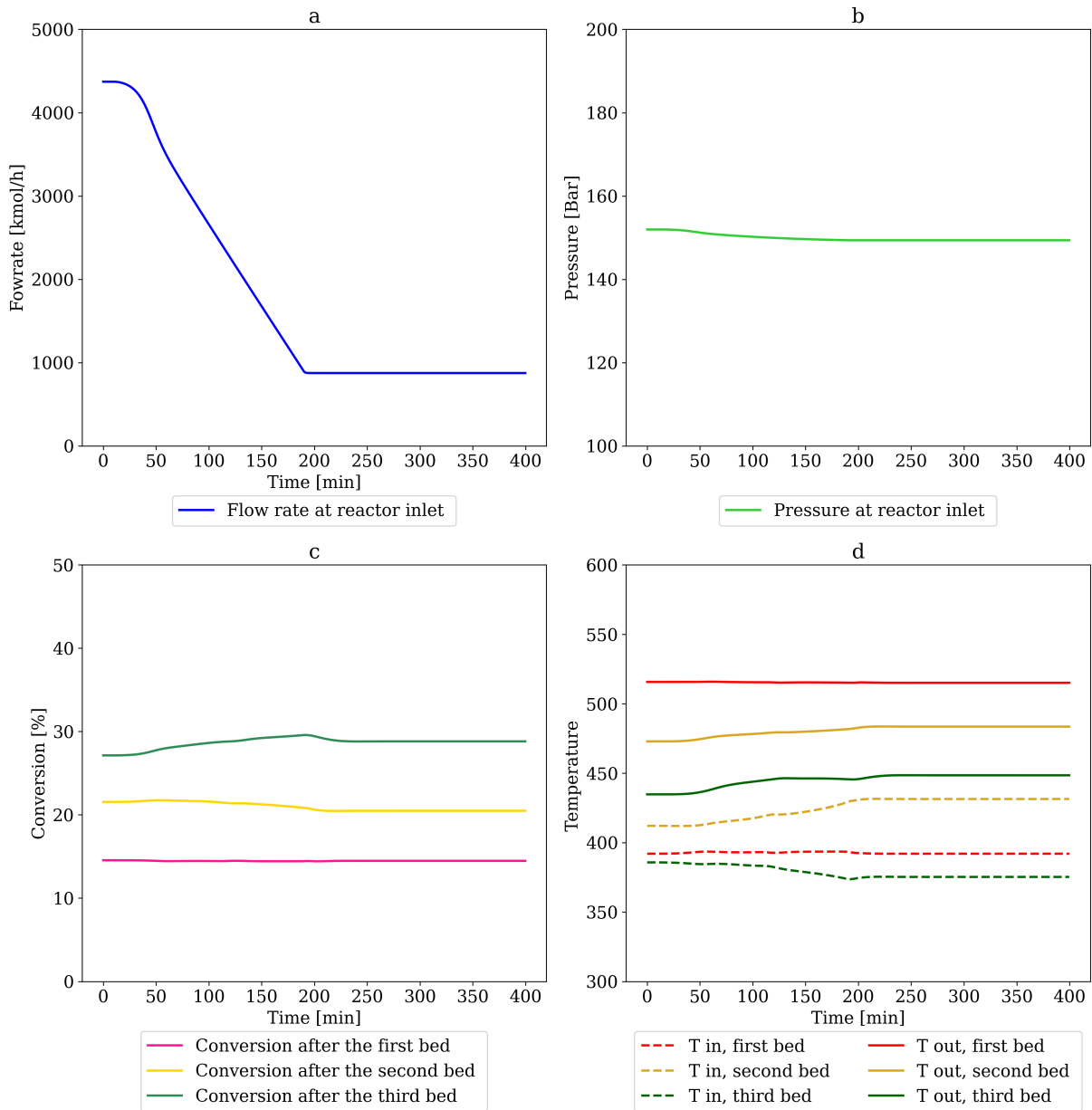


Figure 4.7: Partial simulation (reactor, feed effluent heat exchanger, and waste heat boiler). Results of a load reduction from 100 to 20% in three hours with a temperature control structure that includes two controllers.

Similar results are reported when the flow rate is increased, visible in Figure 4.8. The flow, in this case, is increased from 20% to 100% in three hours (Figure 4.8 a) the pressure is practically constant as before (Figure 4.8 b). The conversion decreases and the temperatures are back to the initial values, Figure 4.8 c and d. The inlet temperature of the first catalytic bed is constant due to the action of the cold shot control. The others are exactly the contrary of what was seen before.

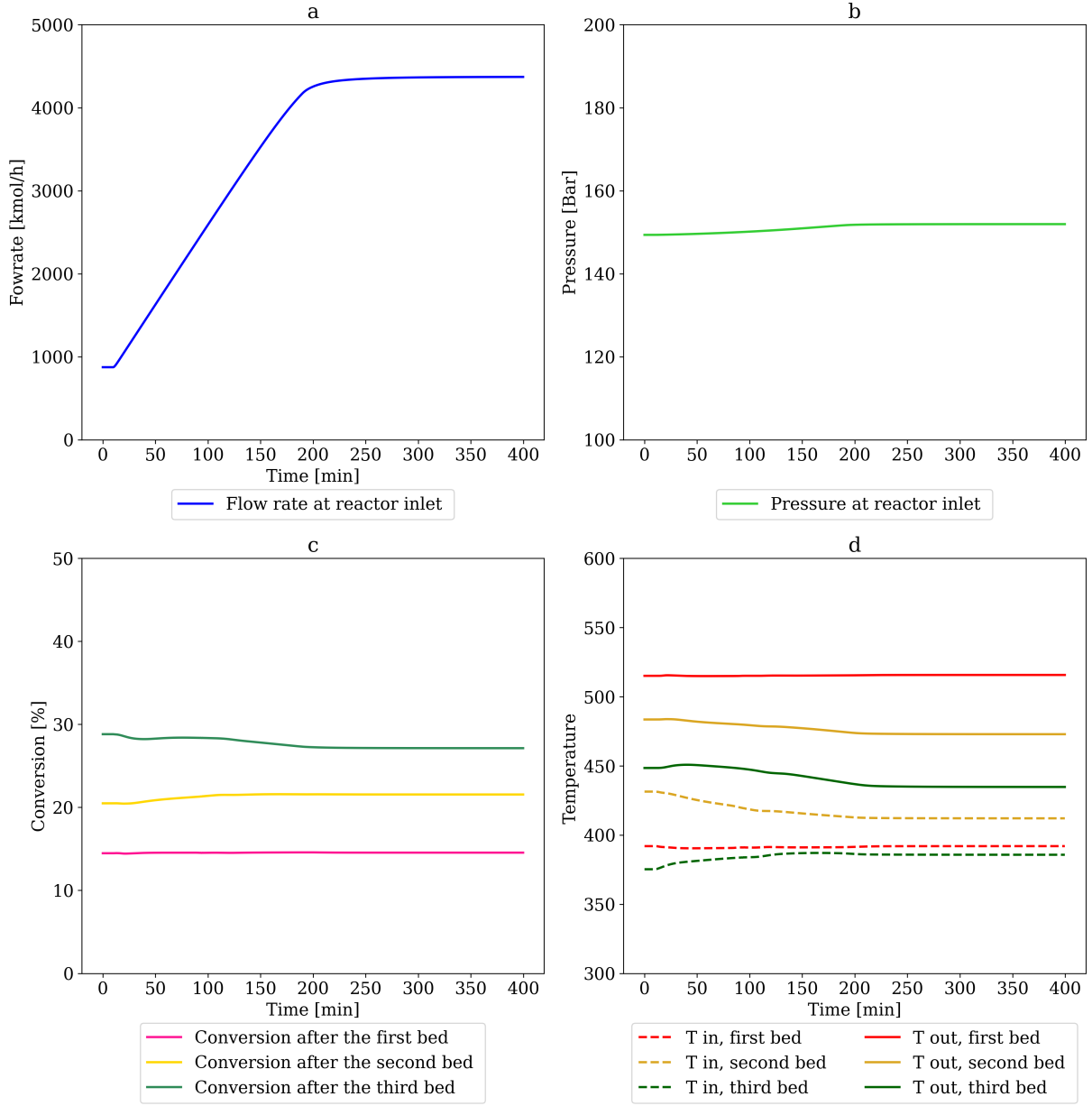


Figure 4.8: Partial simulation (reactor, feed effluent heat exchanger, and waste heat boiler). Results of a load increased from 20% to 100% in three hours with a temperature control structure that includes two controllers.

The tuning of the two controllers was achieved using the SIMC rule, as detailed in Section 2.3. The tuning results are presented in Table 4.1. The SIMC tuning rule was applied based on a graphical deduction of the necessary parameters. Given the satisfactory results, a more complex procedure was deemed unnecessary. In Table 4.1, Δu is the step applied on the manipulated variable, Δy the change in the process variable, k the process gain, τ the process time constant, and Θ the delay. τ_C , K_C , and τ_I are the controller parameters. More details can be found in Section 2.3.

Table 4.1: Tuning parameters for temperature control in the reactor, wherewith WHB is intended the control on the WHB bypass, and with CS the one on the cold shot flow rate.

	Δu	Δy	k	Θ	τ	τ_C	k_C	τ_I
WHB	3%	3.07 °C	1.023 °C/%	0.0 min	0.3 min	0.3 min	0.977 %/°C	0.3 min
CS	2.05%	-1.31 °C	-0.64°C/%	0.0 min	0.3 min	0.6 min	0.782%/°C	0.3 min

To summarise, when the load is decreased, the heat exchangers are more efficient than needed, increasing the hot temperatures and decreasing the cold ones. The residence time in the reactor is increased, which increases the conversion and therefore the outlet temperatures. To maintain the temperatures in the catalyst operating range, two controllers are required. A better temperature control on the reactor could be obtained by optimizing the inlet temperature to the first catalytic bed as in [46].

4.3. Complete System and Pressure Control

As discussed in Section 4.1, when the load decreases, the pressure decreases as well. The need for a pressure control coupled with the temperature one, especially when the makeup gas is reduced by more than -40%, is also reported in [48], and underlined for green ammonia synthesis in [1, 2].

One of the most straightforward methods to control the pressure is to change the compressor speed (and, consequently, duty) [48, 49]. This option, reported in Figure 3.10 has been simulated and the results are reported in Section 4.3.2. In Section 4.3.3 the option of having two lines around the recirculating compressor, one working as antisurge, and one as pressure control [1], is considered as schematized in Figure 3.11. In Section 4.3.4 the option of controlling the pressure through a valve along the synthesis loop has been considered, initially using a valve positioned along the recycle stream valve [35] as in Figure 3.12, later using a valve after the recirculating compressor[1], as in Figure 3.13.

4.3.1. Tuning Results for Different Pressure Control Methods

The process parameters obtained from the simulation and the tuning parameters calculated with the SIMC tuning method (Section 2.3) are summarised in Tables 4.2 and 4.3, where they differ for the manipulated variable used to control the pressure:

- method 1 uses the compressor speed,

- method 2 uses the second antisurge line,
- method 3a uses the recycle valve,
- method 3b uses the valve after the compressor.

When the K_C value is negative, the controller will be set on 'direct', as explained in Section 3.3. When looking at the step response for tuning purposes, an inverse response has been reported for all the cited pressure control methods. This is coherent with what was reported by Gullberg et al. [48]. For tuning purposes, the inverse response time has been included in the delay. The tuning is based on graphical results, and could therefore be improved.

Table 4.2: Process parameters for pressure control tuning.

	Δu	Δy	k	Θ	τ
1	-50 rpm	82.9 kPa	-1.66 kPa/rpm	0.8 min	10.2 min
2	+2 %	213 kPa	106.4 kPa/%	0.4 min	13.9 min
3a	-5 %	34.1 kPa	-6.82 kPa/%	0.4 min	5.6 min
3b	-5 %	65.4 kPa	-13.12 kPa/%	0.4 min	7.4 min

Table 4.3: Controllers parameters for pressure control tuning.

	τ_C	k_C	τ_I
1	3.2 min	-1.54rpm/kPa	10.2 min
2	0.4 min	0.16 %/kPa	3.2 min
3a	0.8 min	-0.68 %/kPa	4.8 min
3b	0.8 min	-0.47 %/kPa	4.8 min

4.3.2. The use of the Compressor Speed for Pressure Control

The compressor speed (or duty) has been reported as an effective manipulated variable for pressure control [48, 49]. The results of applying this pressure control method (added with the temperature control discussed in Section 4.2) when the makeup gas load is decreased from 100 to 20% in three hours are reported in Figure 4.9. The pressure at the reactor inlet is shown in subplot b, and it is evident that this method is very effective. This is

consistent with what was reported in [48], where the control strategy was tested against a step reduction of -20% and still gave particularly good results. In the present work, the makeup gas decrease is gradual, as it has been considered closer to what could happen in a green ammonia dynamic plant.

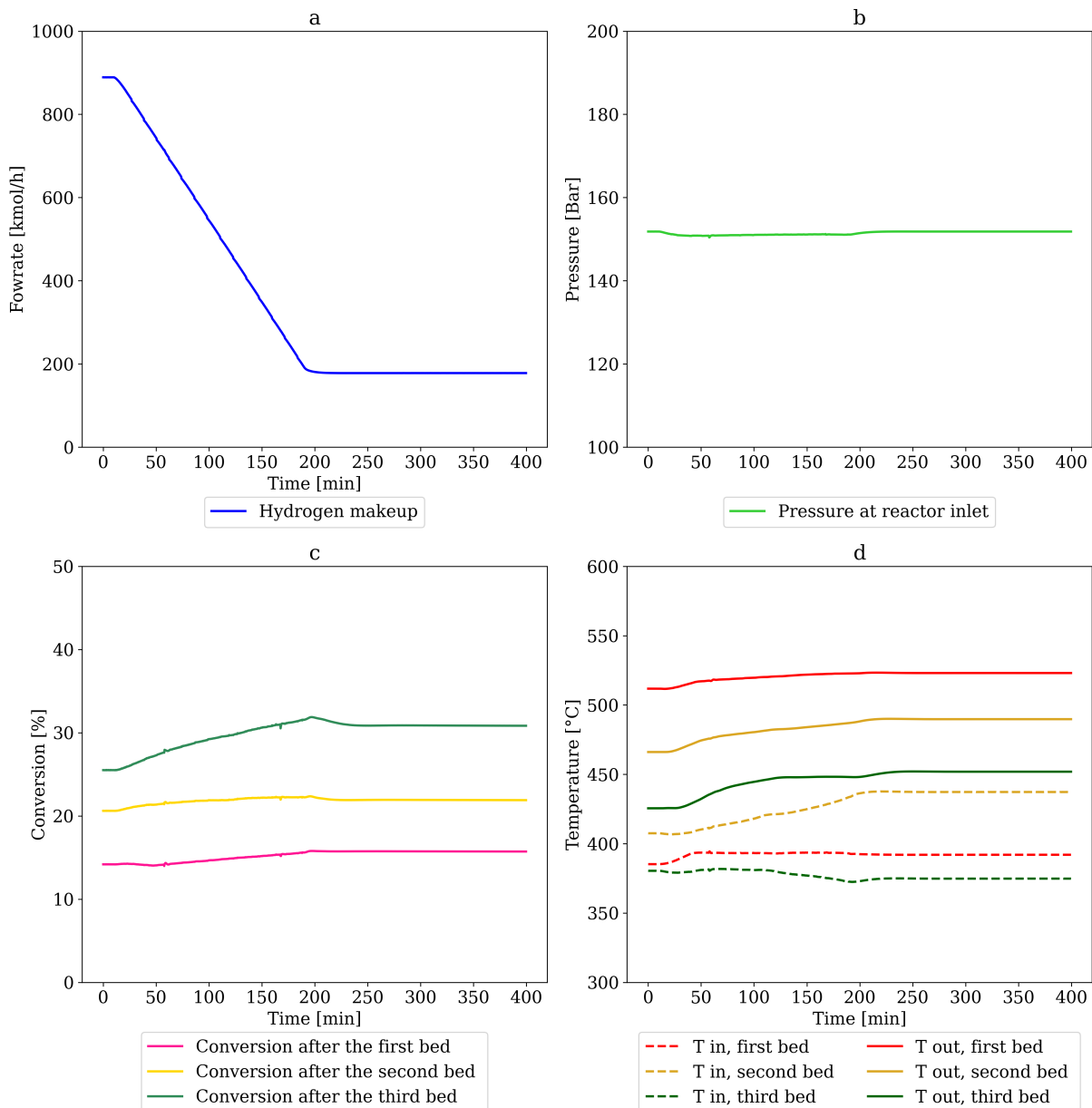


Figure 4.9: Results of a decrease of load from 100% to 20% in 180 minutes, using K-103 speed as pressure control.

There are two main considerations to be carried out regarding these results. First, as previously mentioned, it is important to underline that the curves used to model the compressors have a limited range of speed, as shown in Figure 3.5. When needed, as

in this case, UniSim extrapolates the curves at different rotational speeds, allowing the compressor to operate outside the speed range in the given curves, even if it could affect the accuracy of the results. In this case, the rotations per minute are decreased from 6400 to 945, as it is possible to observe in Figure 4.10. If the specific characteristic curves are supplied, one could study the pairing of two control methods for pressure: the compressor speed and one of the following methods, which could be used when the speed limit is reached. The second, and possibly the main drawback of this method, is the capital cost associated with not having a single-shaft machine, which is usually avoided in industrial practice [2, 28].

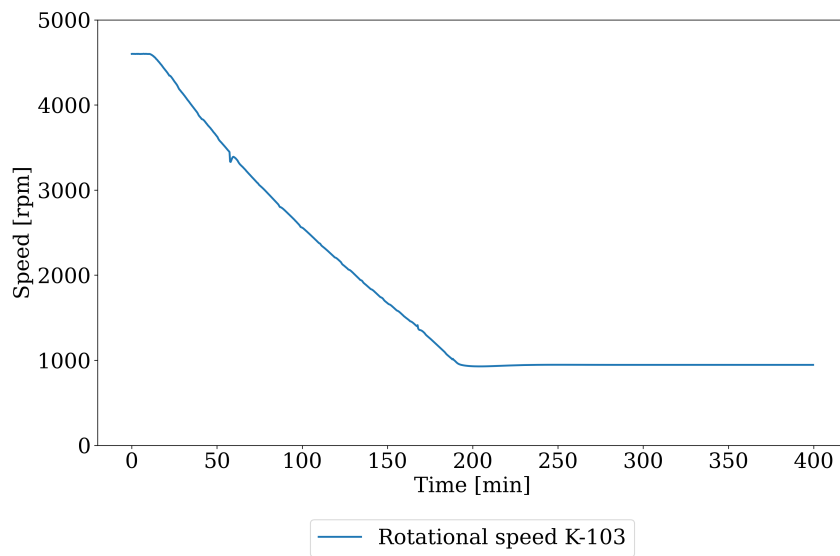


Figure 4.10: K-103 rotational speed when the load is decreased from 100 to 20% in three hours, and the speed is used as manipulated variable for pressure control.

Observing the rest of Figure 4.9, it is notable that maintaining constant pressure allows for almost stable conversion and temperature, as shown in subplots c and d, respectively. It is also noticeable that there is a difference between the maximum values of temperature and conversion reached in this graph compared to the values in the partial simulation (Figure 4.7) which is attributable to the separation and recycle, and will be analyzed in more detail in Section 4.4.

4.3.3. The use of a Second Antisurge Line for Pressure Control

In this section, the results of using two lines around the compressor, as in Figure 3.11 have been reported.

The results of a load decrease from 100 to 20% in three hours are reported in Figure

4.11. The pressure, subplot b, decreases by about 10 bar before the controller's action is effective. When looking at the temperature and conversion in the system, it is possible to observe that the decrease in pressure causes a decrease in the conversion, and, therefore, in the temperature. This explains why, when the pressure decreases, the conversion tends to increase less than what was previously observed (Section 4.2), to then grow again when the pressure is recovered.

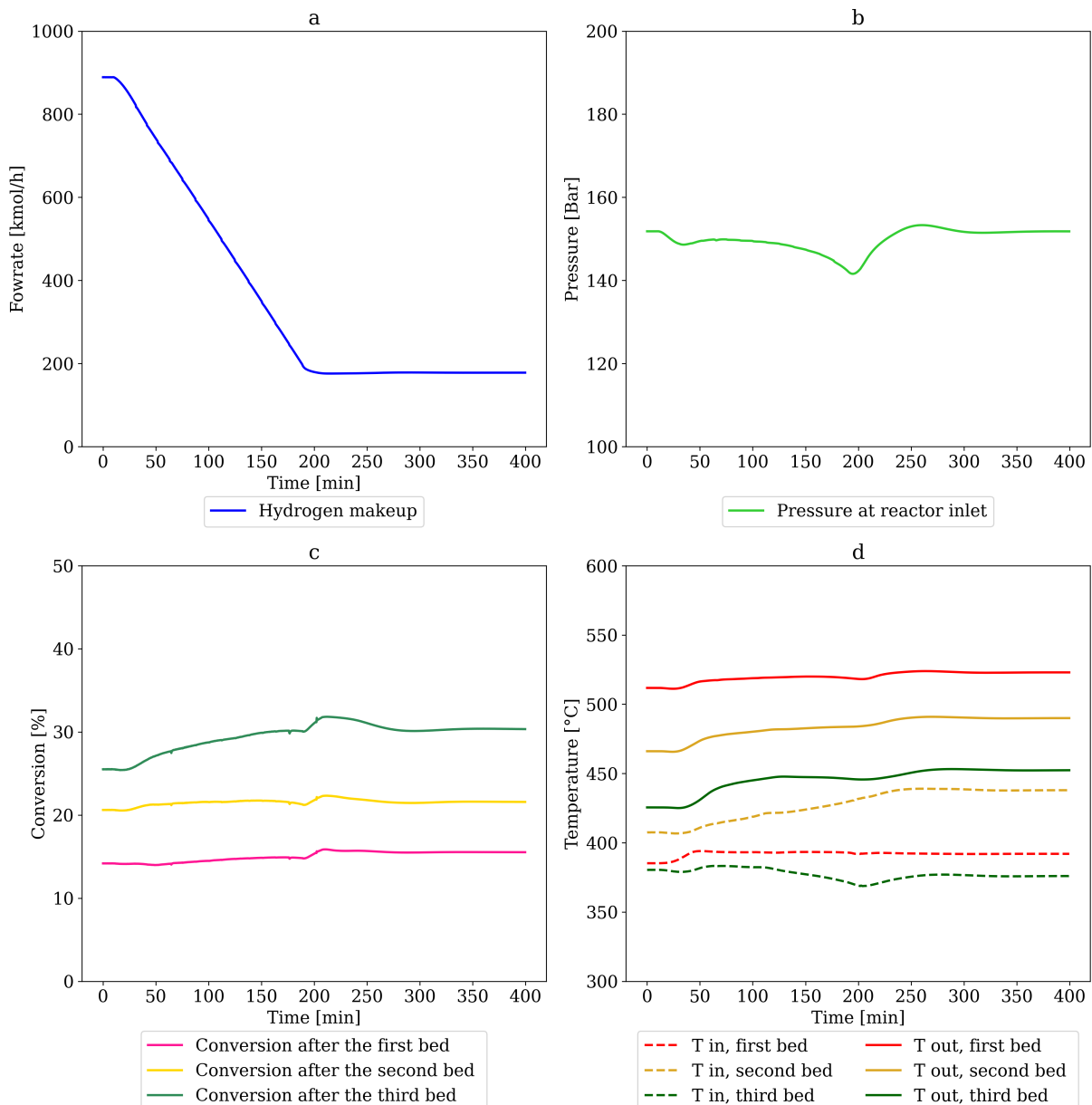


Figure 4.11: Results of load decrease from 100 % to 20% in 180 minutes, using an additional line around the compressor as pressure control.

To maintain the pressure in the system, the valve around the compressor opens, coherently

with what is reported in [1, 2]. This line will here be called the pressure control line. The flow rate in this valve is observed in Figure 4.12, and it reaches values of 77.5 kg/s. To compare, the mass flow of gas entering the reactor at 100% load is 11.65 kg/s. This seems to be a very large value. However, there could be two reasons for this. First, the valve opens so that less amount of gas is sent to the reactor, in the attempt to keep the amount of gas in the loop, and therefore the pressure, constant [1, 2]. Moreover, the pressure drop in the system decreases significantly when the flow is reduced, as it is proportional to the velocity squared. This implies that the compressor will deliver a smaller pressure increase, which, when keeping the speed constant, could increase the flow.

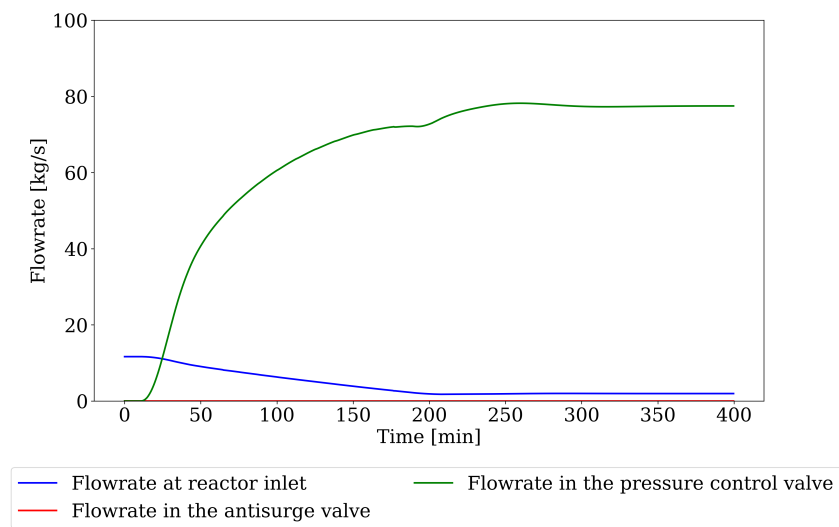


Figure 4.12: Flow rate in the pressure control line, parallel to the antisurge, when the load is reduced from 100 to 20% in 180 minutes.

When the load is increased similar considerations can be carried out. Figure 4.13 shows the results when the load is increased. In graph a, the hydrogen makeup can be observed, which increases from 20 to 100%. the pressure can be observed in Graph b. It mirrors the behavior previously observed. It increases initially, then decreases thanks to the controller action. Also, the conversions (graph c) mirror the previously observed behavior. The same is valid for the temperatures, which go back to their original value, with a small increase in the first minutes, due to the higher pressure in the reactor. This method overall works, even though it could probably be improved with the use of feedforward control, as suggested in [2]. Moreover, when the reduction happens in a lower amount of time, for instance, one hour, the pressure drop will be higher, as reported in Appendix D.1. Therefore particular attention should be given not to have a drastic decrease in load in the system.

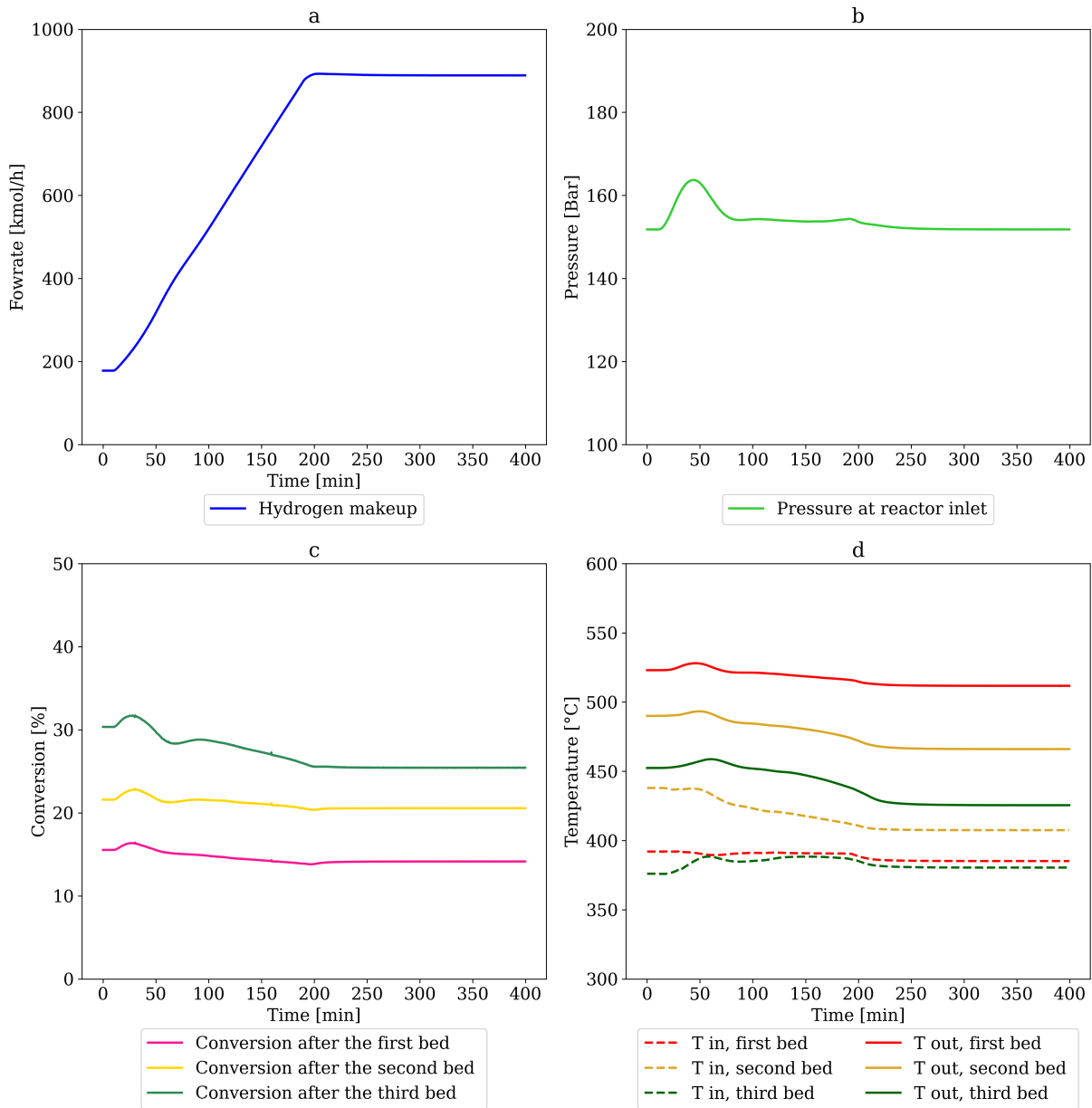


Figure 4.13: Results of an increase of load from 20 % to 100% in 180 minutes, using an additional line around the compressor as pressure control.

4.3.4. The use of a Valve in the Loop for Pressure Control

This section considers the use of a valve in the loop as a pressure control. As explained in Section 2.3.2, this option has been considered by Koschwitz et al. [35] by using a valve on the recycle stream, and by Topsoe [1] by using a valve after the compressor.

The use of the recycle valve for pressure control

In this section the results of using the recycle valve as pressure control, as suggested in [35] are reported. The results are visible in figure 4.14.

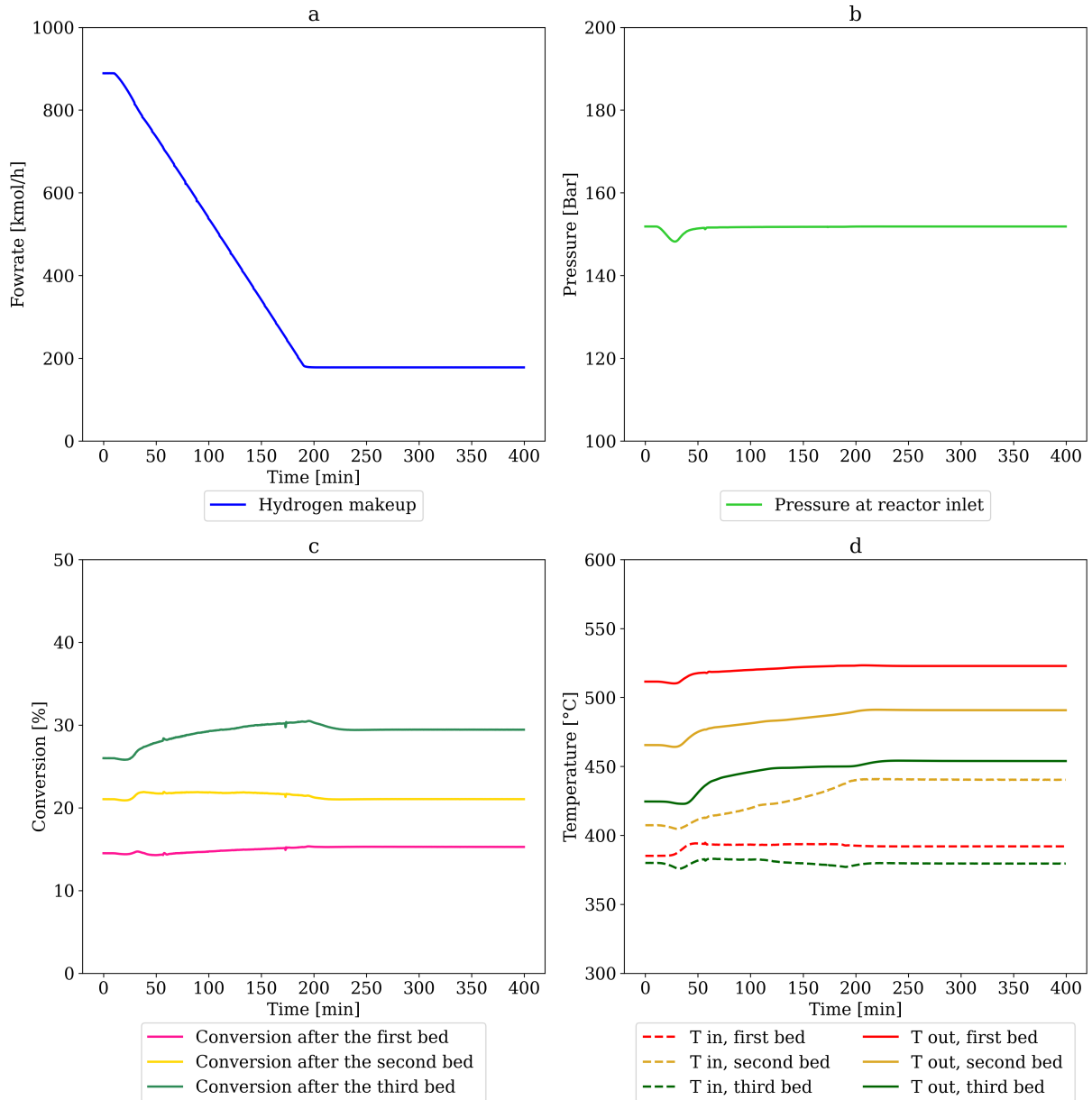


Figure 4.14: Results of a decrease of load from 100% to 20% in 180 minutes, using a valve in the recycle stream as pressure control.

The simulation in this case yields better results than the one exposed in the previous Section. The valve in the recycle line closes from 100% to 3.59%. These numbers mainly depend on how the valve is sized, therefore, if needed, one could resize the valve.

The pressure in the system is therefore controlled by decreasing the recycle gas flow. This could be working for two reasons. First, the gas is retained in the reactor, which maintains the pressure [1]. Second, slowing the amount of gas that enters the reactor decreases the number of moles converted into ammonia, which, since the reaction happens with a decrease in the number of moles, helps in avoiding a pressure decrease.

It is also interesting to observe the stream in the antisurge valve which, logically, is way less than what was observed before. This is reported in Figure 4.14

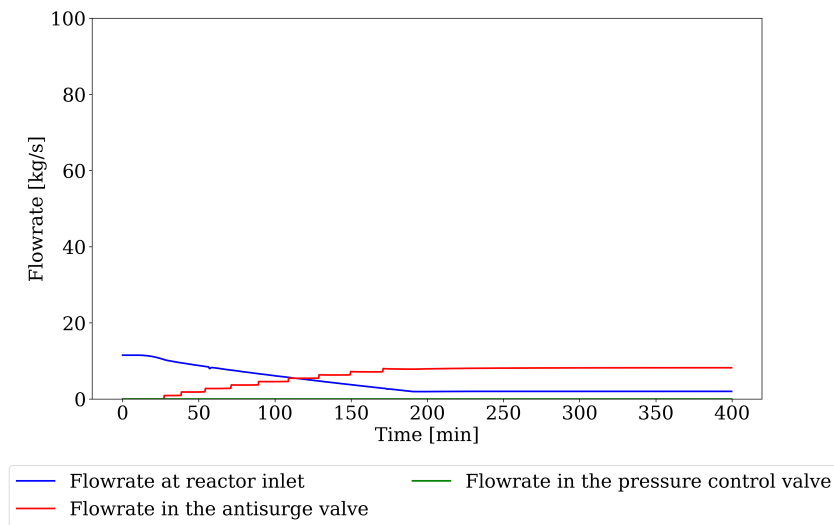


Figure 4.15: Flow rate in the antisurge line, when the load is reduced from 100 to 20% in 180 minutes, and the recycle valve is used as pressure control. The y-range is kept as in Figure 4.12 to facilitate the comparison.

The use of the valve after compressor for pressure control

The results of controlling the pressure with a valve situated after the compressor K-103 are reported in Figure 4.16.

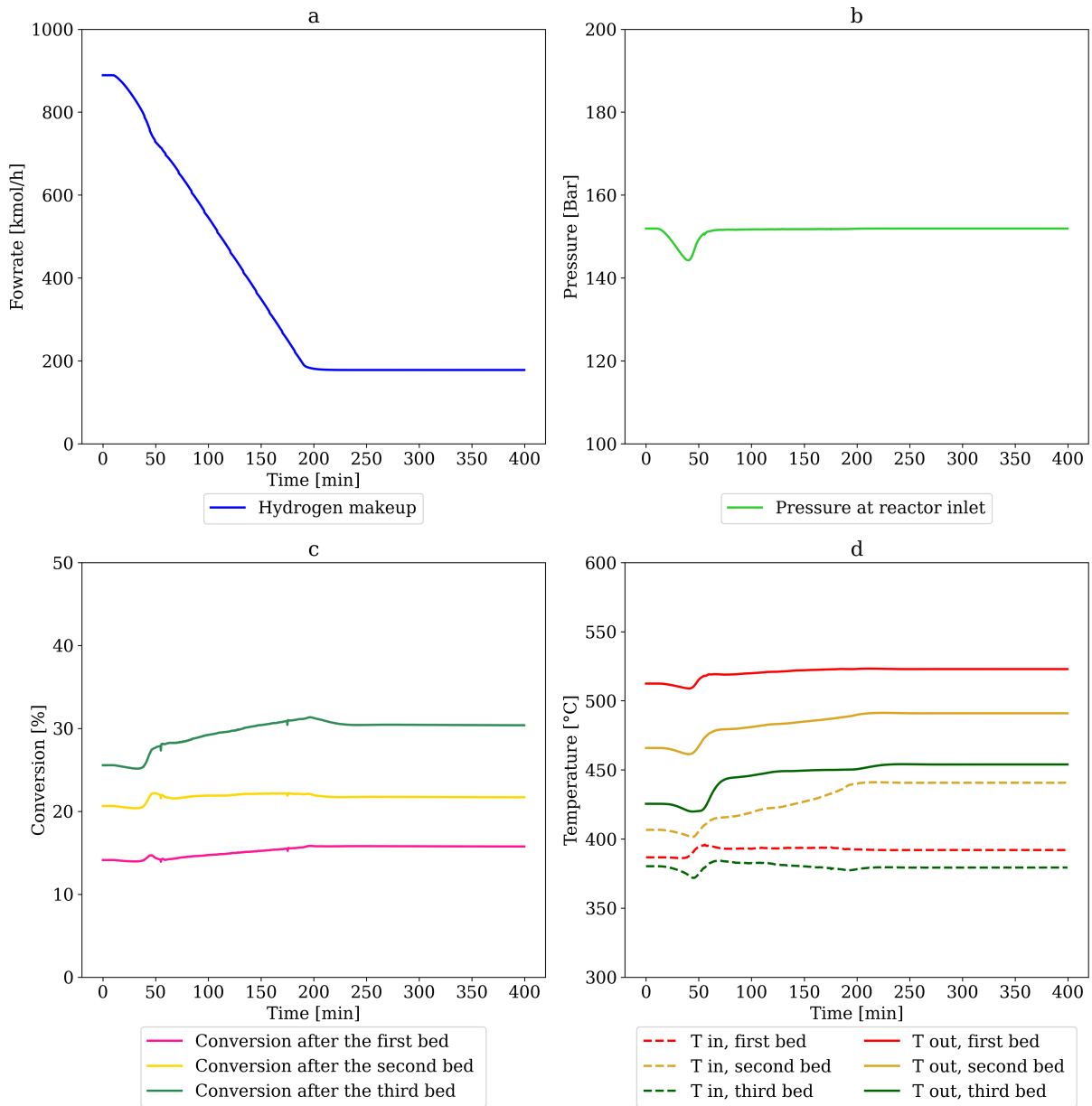


Figure 4.16: Results of a decrease of load from 100% to 20% in 180 minutes, using a valve in after the compressor as pressure control.

In this case, the valve closes from 100 to 2.63%. The results are very similar to the ones obtained in Section 4.3.4. This is logical as it works in the same way: by decreasing the flow rate in the loop. According to [1] this method is particularly useful in the case of sudden decreases. One of the possible drawbacks of having a valve in the loop is the associated pressure drop in the valve.

4.4. Temperature Control on the Separation and its effect on the Overall Plant

As previously discussed, the temperature in the separation section affects the rest of the system. To analyze this, a case in which the temperature in the separation section is controlled was simulated. The control structure added is the one schematized in Figure 3.14, and the tuning parameters are listed in Table 4.4.

Table 4.4: Tuning parameters for control structure employed in the separation section.

	Δu	Δy	k	Θ	τ	τ_C	k_C	τ_I
HX-107	-20%	3.45 °C	-0.17 °C /%	0 min	0.17 min	0.33 min	2.89 %/°C	0.17 min
HX-108	-20%	0.45 °C	-0.02 °C /%	0 min	1.67 min	33.4 min	2.24 %/°C	1.67 min

In Figure 4.17 the results of having or not this additional control are compared for a reduction of 50% load in two hours. In subplot (a), the temperature in the separation section is shown. In the case of a load reduction without control of the separation temperature, this temperature decreases as the coolers are designed for higher loads. This reduction, in turn, decreases the concentration of ammonia in the recycle, as observed in the second subplot (b). The decrease in ammonia percentage in the recycle and, therefore, in the reactor feed, thermodynamically favors the reaction. This increases the conversion in the first catalytic bed and, consequently, the temperature, as shown in subplots (c) and (d) respectively. In the previous sections, it became evident that the highest temperatures were recorded at the outlet of the first catalytic bed. Considering that particular attention should be given to the reactor temperature in green ammonia synthesis, especially when the plant operates at low load for a prolonged time, as this could cause catalyst overheating [24], these considerations are particularly interesting. It is noteworthy that an effective way to reduce catalyst overheating is to increase the temperature in the separation section. This increases the ammonia percentage in the recycle and reduces the highest temperature in the converter, thereby preserving the catalyst. This consideration is also reported by Topsoe [1] and it is coherent with what is reported in [30], as they model that a change in the separation temperature will affect the operating conditions in the reactor. However, Koschwitz et al. [35] advise against an increase in the condensation temperature. They analyze this case as a possible malfunction of the temperature control

on the separator temperature and affirm that increasing the temperature will decrease the flow in the recycle, thereby increasing the power input to the compressor. This should be taken into consideration as a drawback of the proposed method even though Koschwitz et al. [35] have very good control of the temperature in each bed of the reactor. They utilize a temperature control on each reactor bed which combines electrical heating and air cooling, a method that can be applied in small-scale ammonia production, and it is not therefore considered in this thesis.

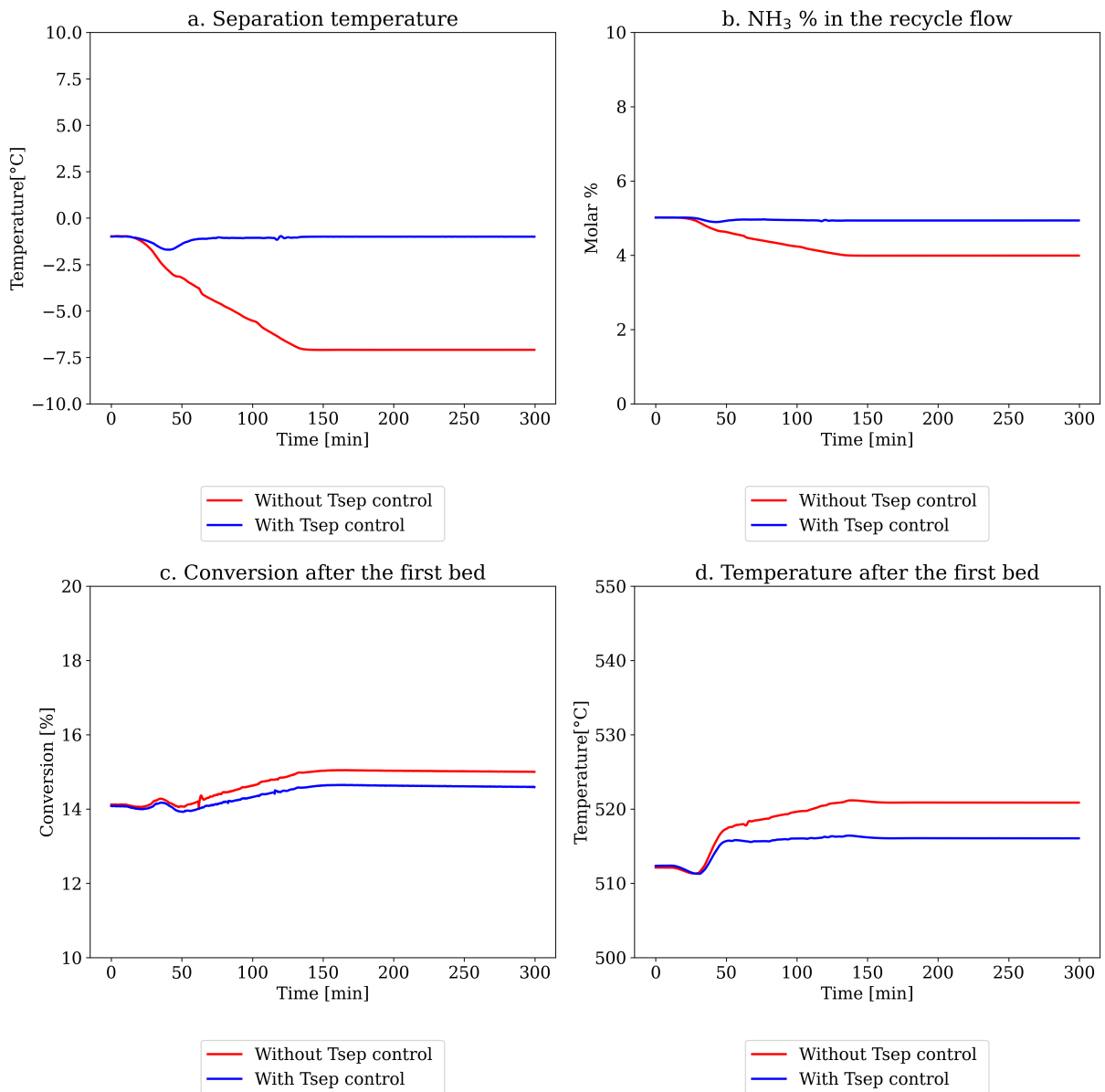


Figure 4.17: Load reduction of 50% in 120 minutes. Comparison between controlling or not the temperature in the separation section.

5 | Conclusions and future developments

In conclusion, this thesis provides the opportunity to examine the dynamic behavior of the system when hydrogen makeup is reduced.

In order to analyze the impact of load reduction on reactor temperature, a partial simulation including only the reactor, feed-effluent heat exchanger, and waste heat boiler was conducted. The reactor model used is a simplified one, in which each catalytic bed is modeled with a packed bed reactor in UniSim. The results indicated that load reduction has two main effects. Firstly, it increases the residence time which can consequently increase the conversion. Secondly, makes the heat exchanger larger than what would be necessary to achieve the design temperatures. Namely, the heat exchangers are sized for 100% loads, which makes them oversized when the load is decreased. To control the reactor temperature a control structure on the waste heat boiler needs to be implemented. One option is to regulate the water flow, and the other, simulated in this project, is to partially bypass the waste heat boiler. Additionally, the cold shot stream, which directs part of the cold feed directly to the first catalytic bed, can prevent catalyst overheating. When these two temperature controls are implemented, the temperature in the reactor appears to remain in the desired range. Furthermore, the separation temperature impacts the reactor conditions. When increased, it will increase the ammonia present in the recycle loop, thereby decreasing the nitrogen conversion in the reactor, which will, in turn, decrease the maximum temperature reached in the reactor. This is particularly interesting in the case of persistent low-load operations of the ammonia synthesis plant, where the catalyst could overheat.

When analyzing the effect of a load reduction on the overall system and its pressure, it is observed that the pressure decreases upon load reduction, which consequently diminishes the conversion and lowers the temperature, potentially leading to system shutdown. Various pressure control methodologies are evaluated. Initially, adjusting the recirculating compressor speed and duty emerges as the most straightforward and effective approach.

However, the applied compressor simulation curves lack specificity for this scenario, as the speed needed to reach the desired pressure follows outside the given range. Thus, employing specific curves within the relevant range would probably increase the accuracy of the results. Moreover, this method could be economically disadvantageous in the case of large ammonia plants, where usually the recirculating compressor is on the same driver as the makeup gas one. Therefore, the recirculating compressor could not vary speed autonomously. Alternatively, other methods entail utilizing the antisurge valve (or its parallel counterpart) or introducing one or more valves within the loop. In the former, the valve opens to increase pressure, while in the latter, it closes. Implementing a valve within the loop appears to yield better results.

The results obtained suggest that it is possible to operate a green ammonia plant at partial loads. There are however some limitations related to the simulation of individual equipment that could be addressed in future work. For instance, the reactor model is here a simplified one, and more work could be carried out to analyze the temperature profiles. Accurate results regarding the compressors and the surge require specific compressors' characteristic curves, which could be used in future work. When considering the control structure, a model predictive control could be studied to improve the control performance, given that the decrease in the hydrogen makeup is not an unforeseen disturbance. Further efforts may include an optimization of the plant and reactor design, which considers its operability at different loads. Moreover, integrating the water electrolysis process would be beneficial as it would allow accounting for typical fluctuations, optimizing the design of the integrated process, and sizing the eventual energy storage required. Finally, the work could be concluded with an economic evaluation that also considers all the mentioned optimization challenges.

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A | Additional Steady State Results

Results

In this chapter, additional steady-state results from previous work that can be useful are reported.

A.1. Kinetic Model Studies

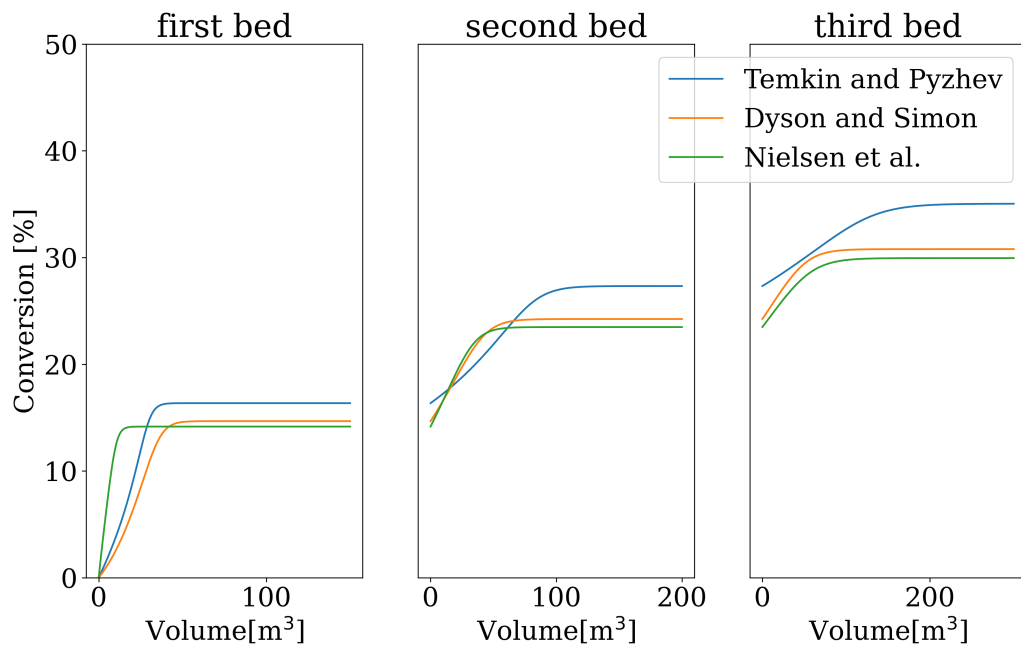


Figure A.1: Comparison of three kinetic models, conversion in each catalytic bed.

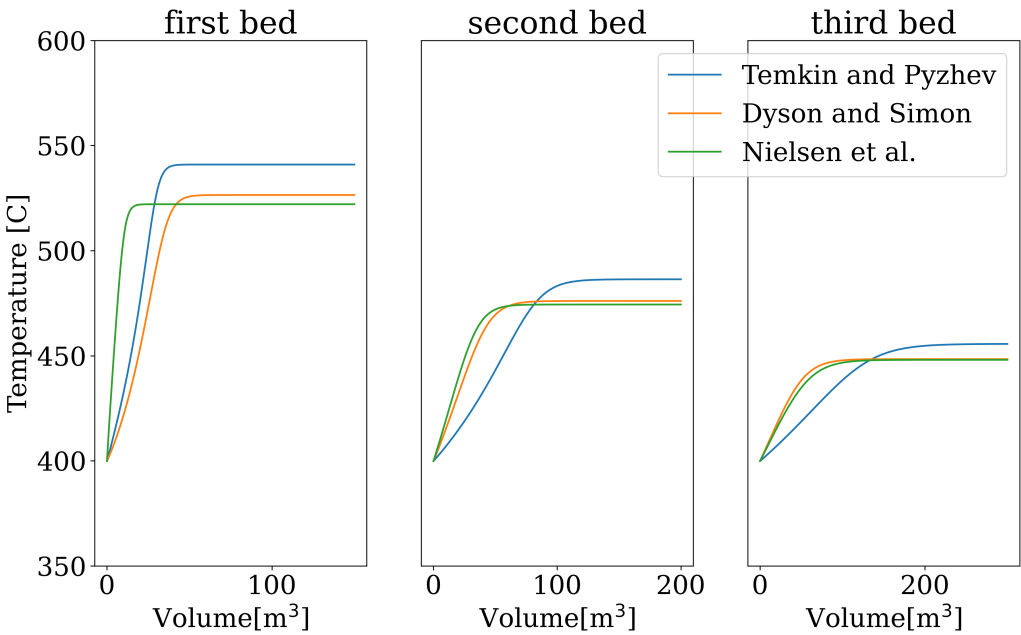


Figure A.2: Comparison of three kinetic models, conversion in each catalytic bed.

A.2. Steady State UniSim Simulation

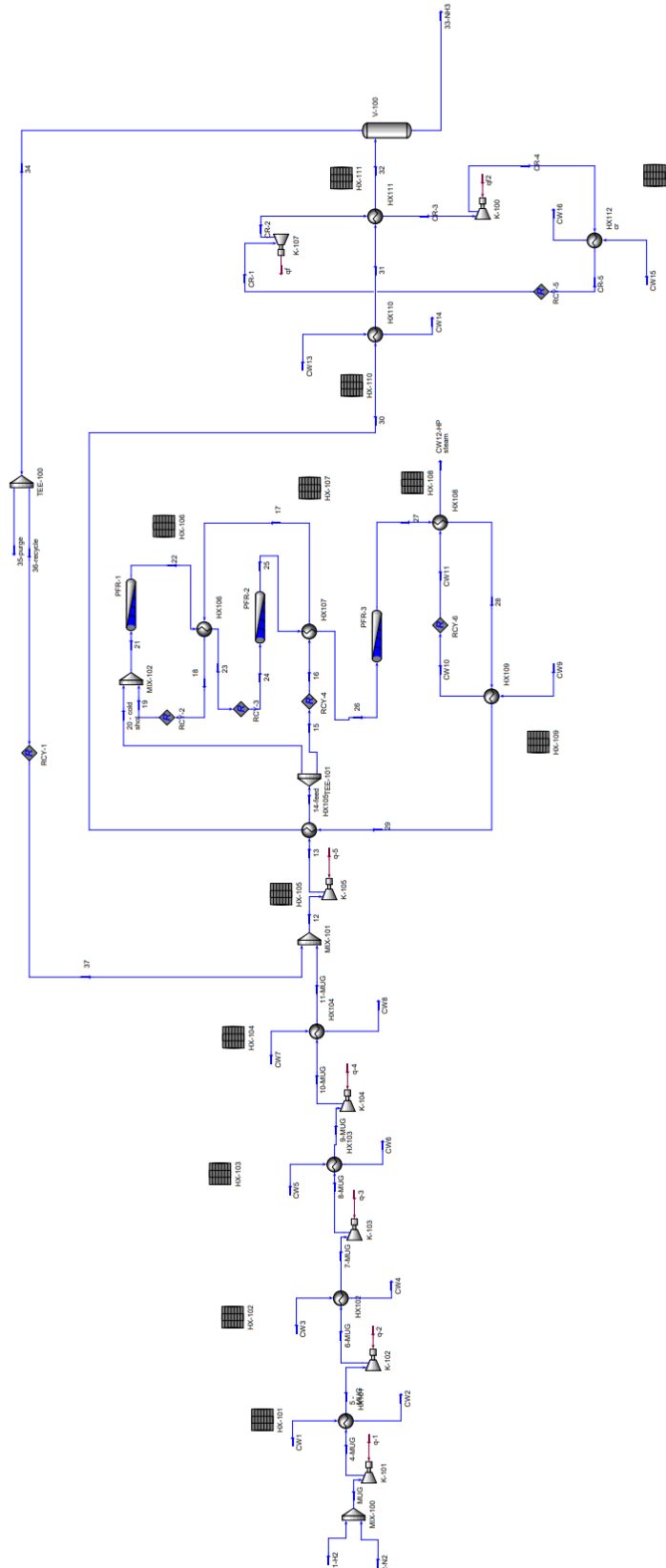


Figure A.3: Steady state simulation carried out in UniSim Design [11]

B | Simulation

In this Appendix the image of the complete simulation, with the flow controllers, antisurge controls, and the level control on the separator is reported.

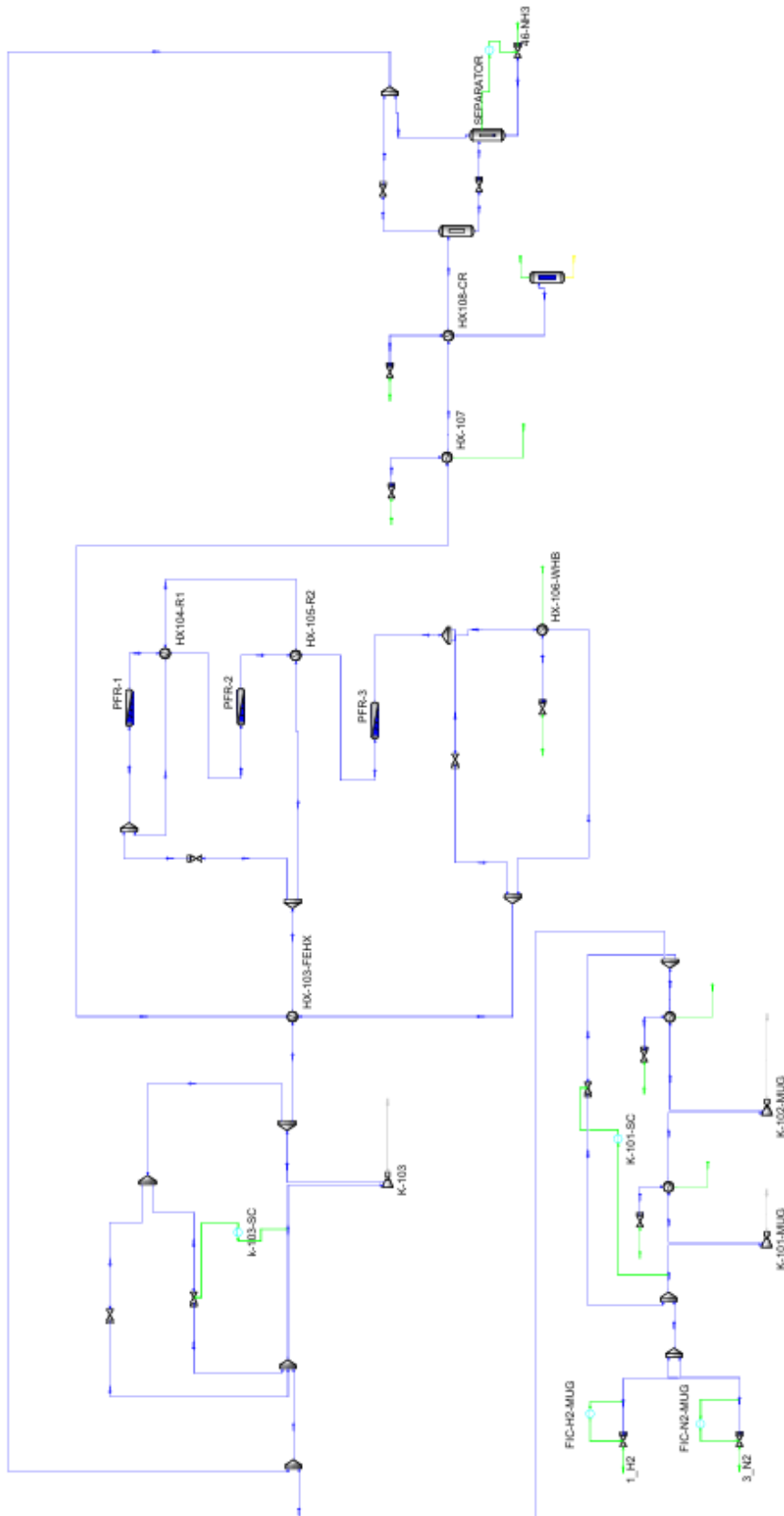


Figure B.1: Dynamic simulation carried out in UniSim Design.

C | Other Tuning Parameters

In this appendix the tuning parameters of the flow controllers and antisurge controllers are reported, as they have not been reported in the text.

C.1. Tuning of flow controllers

In this section, the tuning parameters for the flow controllers are reported. In this simulation, there are four flow controllers. Two antisurge controls, one flow control on the hydrogen makeup flow rate, and one on the nitrogen makeup flow rate. The one on the hydrogen is manipulated to simulate different hydrogen-limited scenarios, the one on the nitrogen to keep the hydrogen-to-nitrogen ratio in the makeup gas at 3. In Tables C.1 and C.2 all the parameters are reported. The meaning of each parameter can be found in Section 2.3.

Table C.1: Process parameters for flow controllers and antisurge tuning.

	Δu	Δy	k	Θ	τ
FIC - H2 - MUG	-2%	-35.85 kmol/h	17.92 kmol/h / %	0.0 min	0.17 min
FIC - N2 - MUG	-2%	-12.94 kmol/h	6.47 kmol/h / %	0.0 min	0.17 min
SC - K101	2%	56.94 m ³ /h	28.47 m ³ /h /%	0.0 min	0.3 min
SC - K103	2%	38 m ³ /h	19.10 m ³ /h /%	0.0 min	0.2 min

Table C.2: Caption of the Table to appear in the List of Tables.

	τ_C	k_C	τ_I
FIC - H2 - MUG	0.17 min	0.056 % h/kmol	0.2 min
FIC - N2 - MUG	0.17 min	0.155 % h/kmol	0.2 min
SC - K101	0.3 min	0.035 % h/m ³	0.3 min
SC - K103	0.25 min	0.04 % h/m ³	0.2 min

The antisurge was added using the UniSim function. The antisurge equation is obtained by interpolation with a polynomial curve of the points at the left (low flow rate) for each speed-defined characteristic curve.

D | Additional Results

D.1. Results of a One-hour time Load Decrease

D.1.1. One-hour Load Changes, Partial Simulation Results

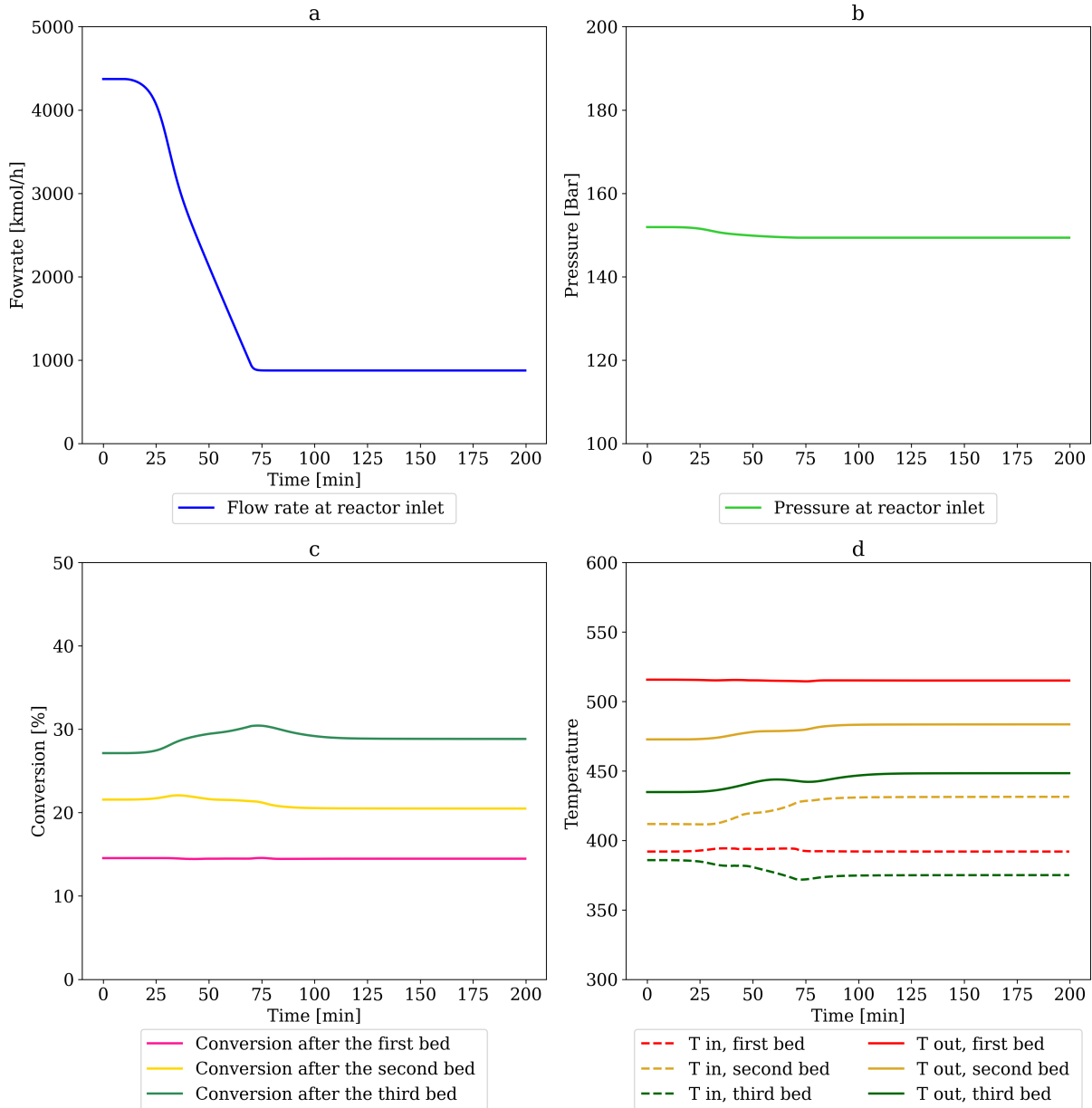


Figure D.1: Results of load decrease from 100 % to 20% in 60 minutes, partial simulation, with two temperature controls.

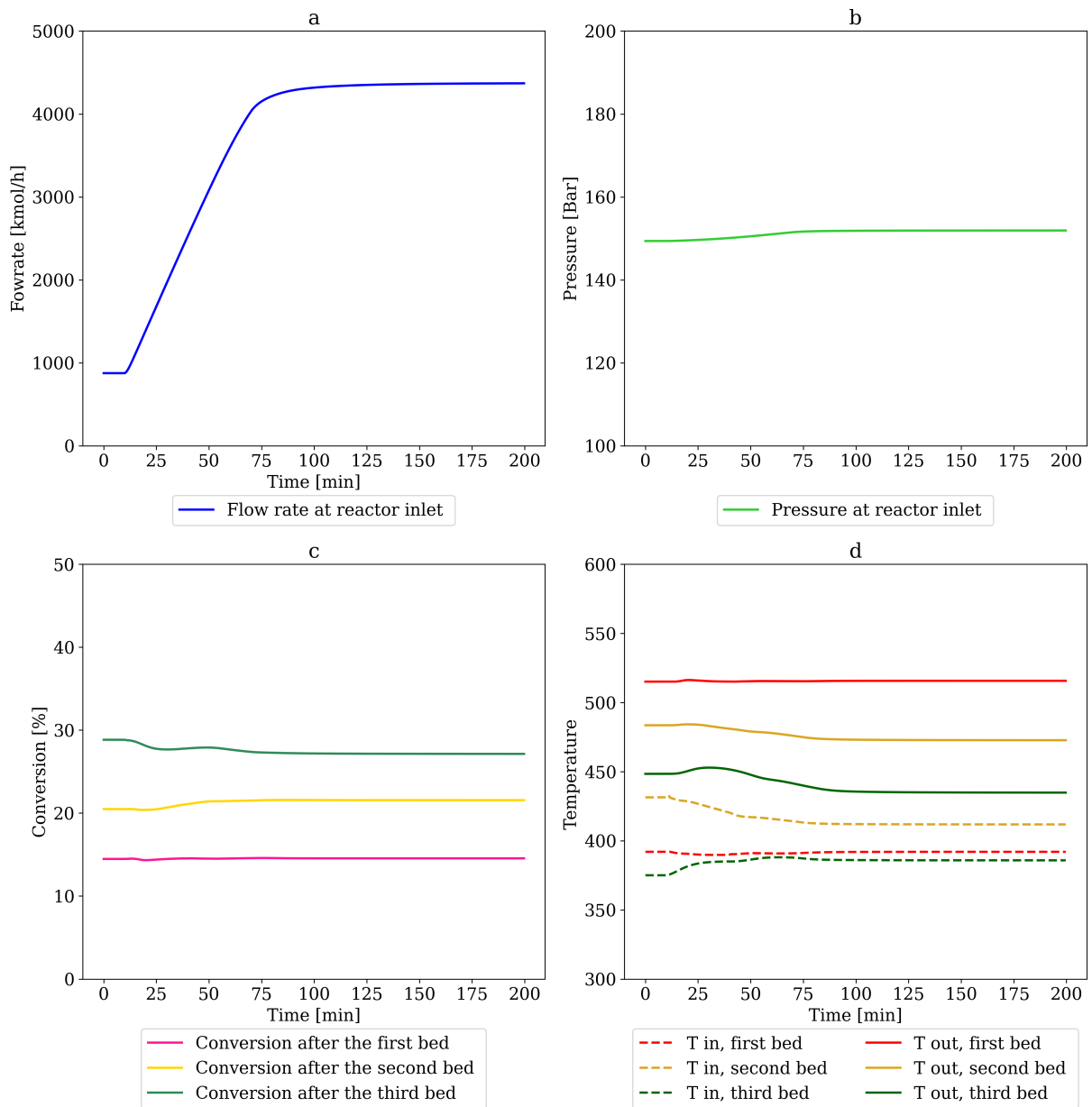


Figure D.2: Results of load increase from 20 % to 100% in 60 minutes, partial simulation, with two temperature controls.

D.1.2. One-hour Load Changes, Complete Simulation Results

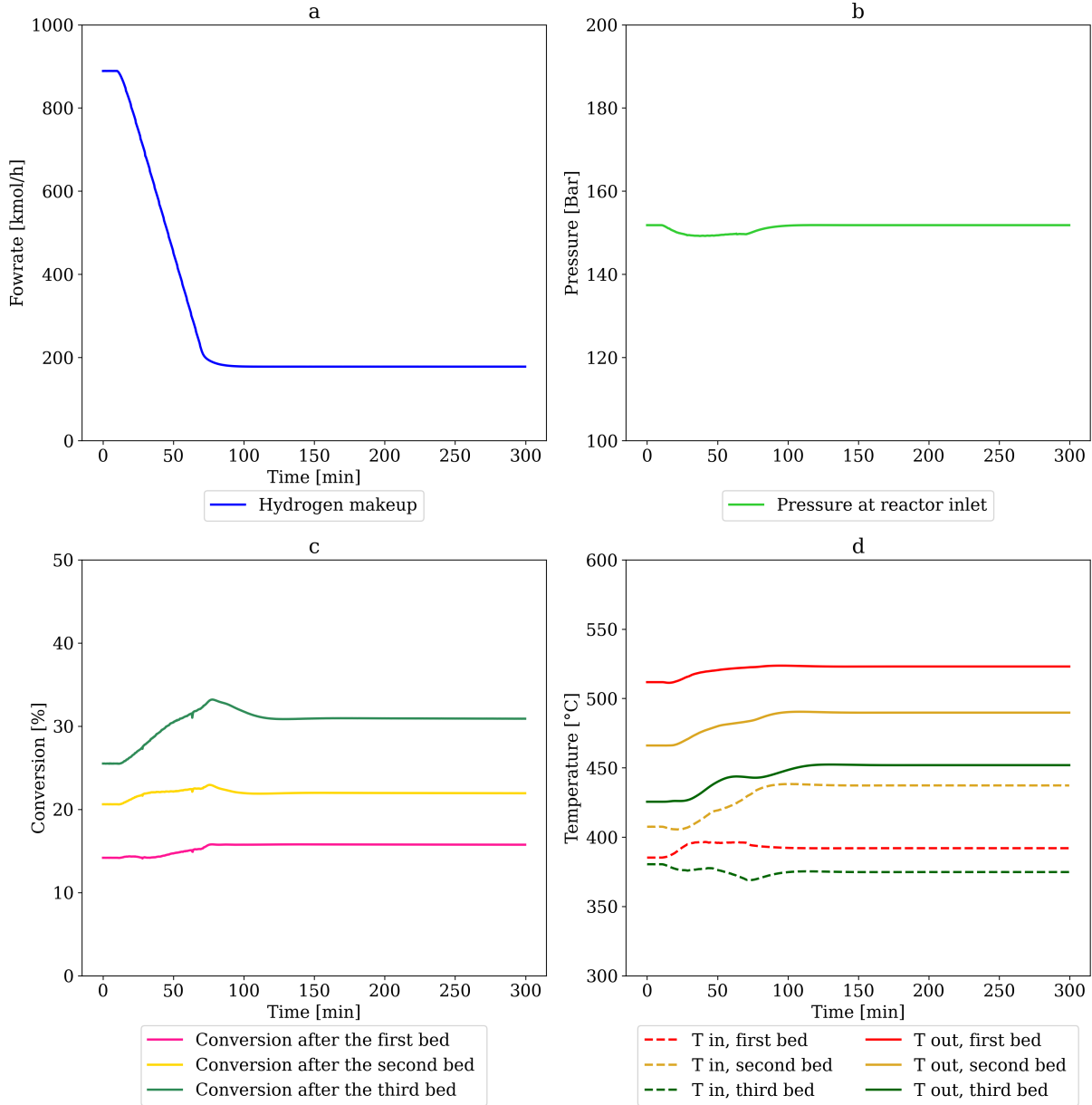


Figure D.3: Results of load decrease from 100 % to 20% in 60 minutes, using the compressor speed compressor as pressure control

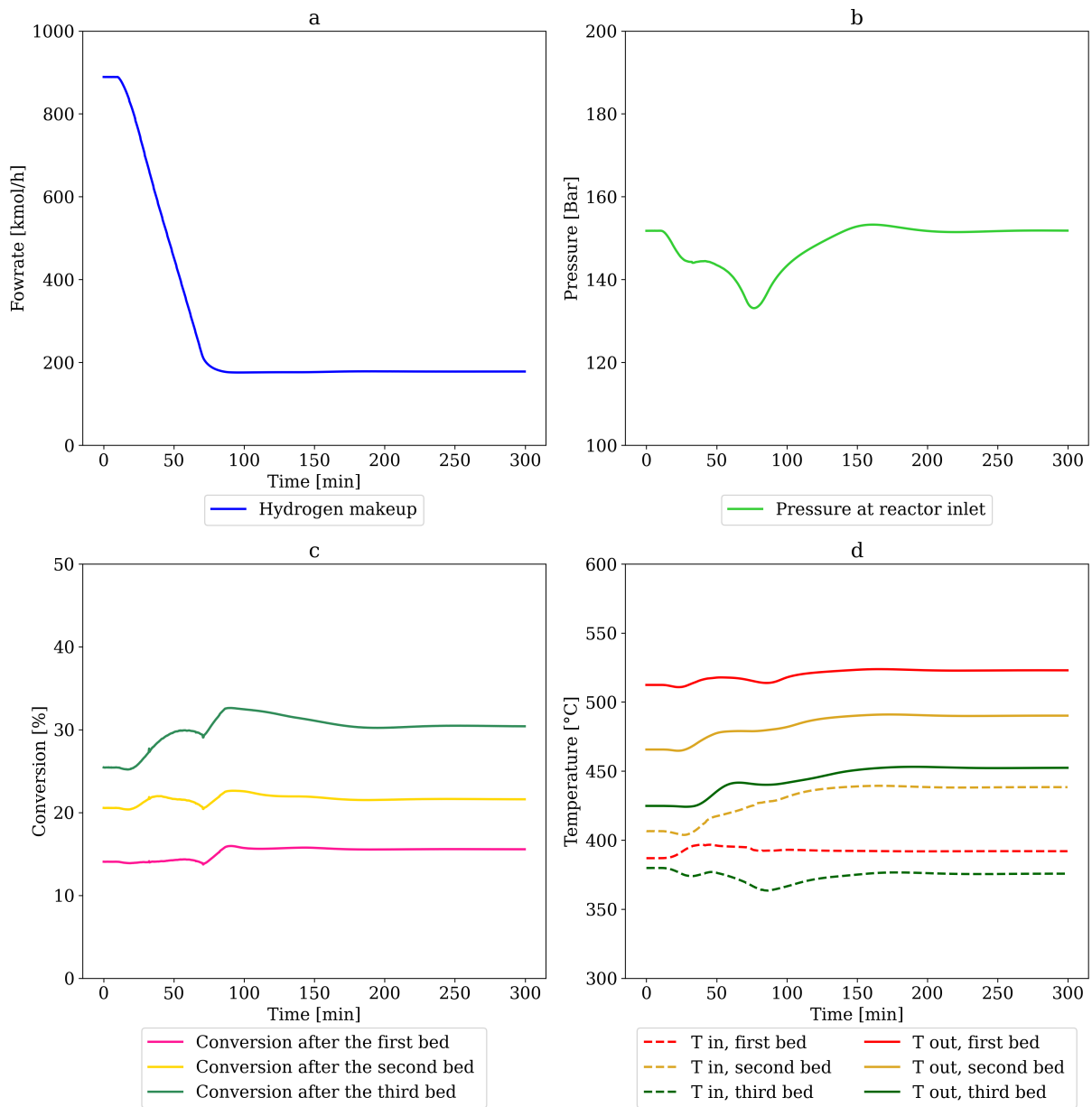


Figure D.4: Results of load decrease from 100 % to 20% in 60 minutes, using an additional line around the compressor as pressure control, tight control

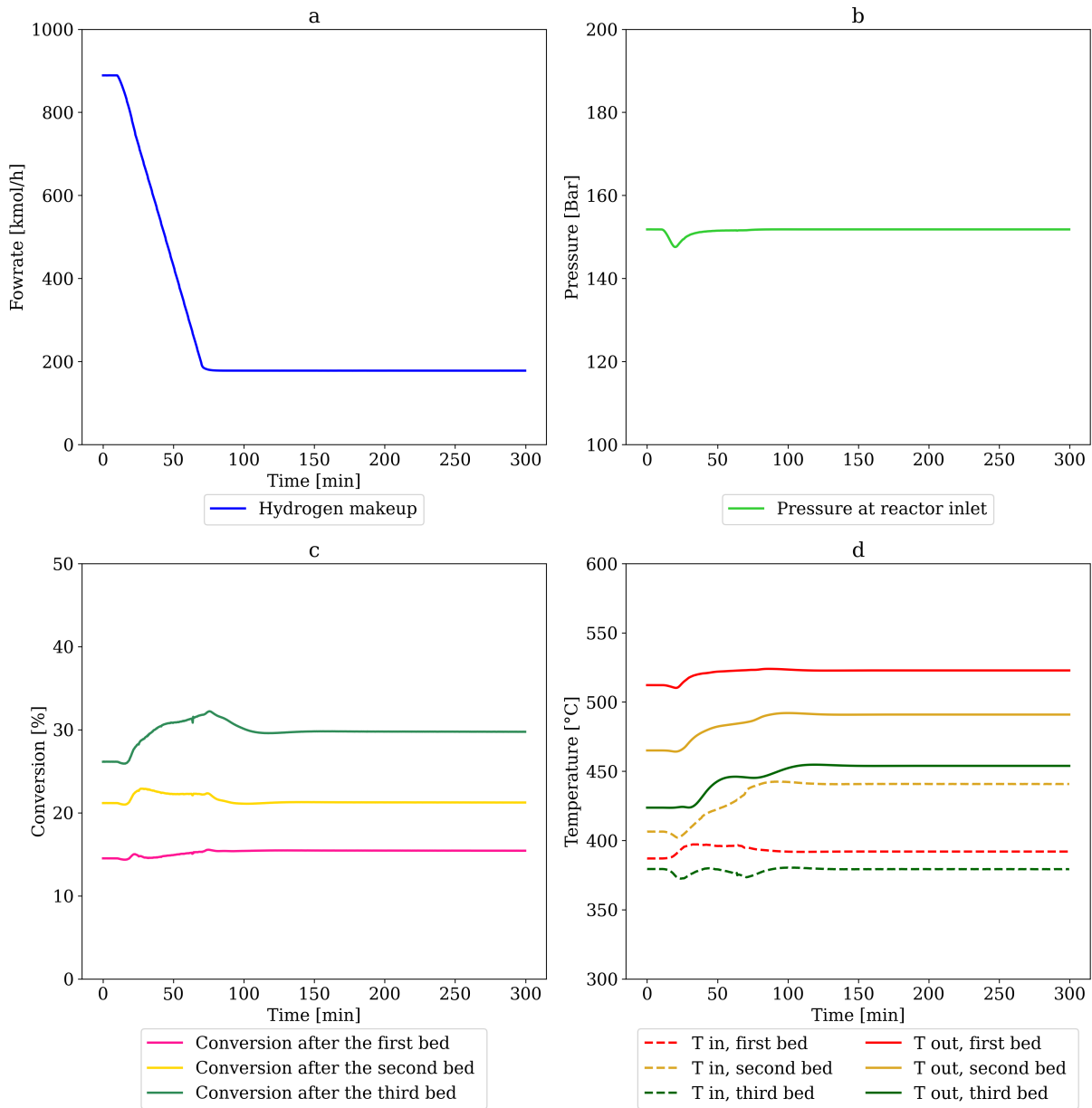


Figure D.5: Results of a decrease of load from 100% to 20% in 60 minutes, using a valve in the recycle stream as pressure control

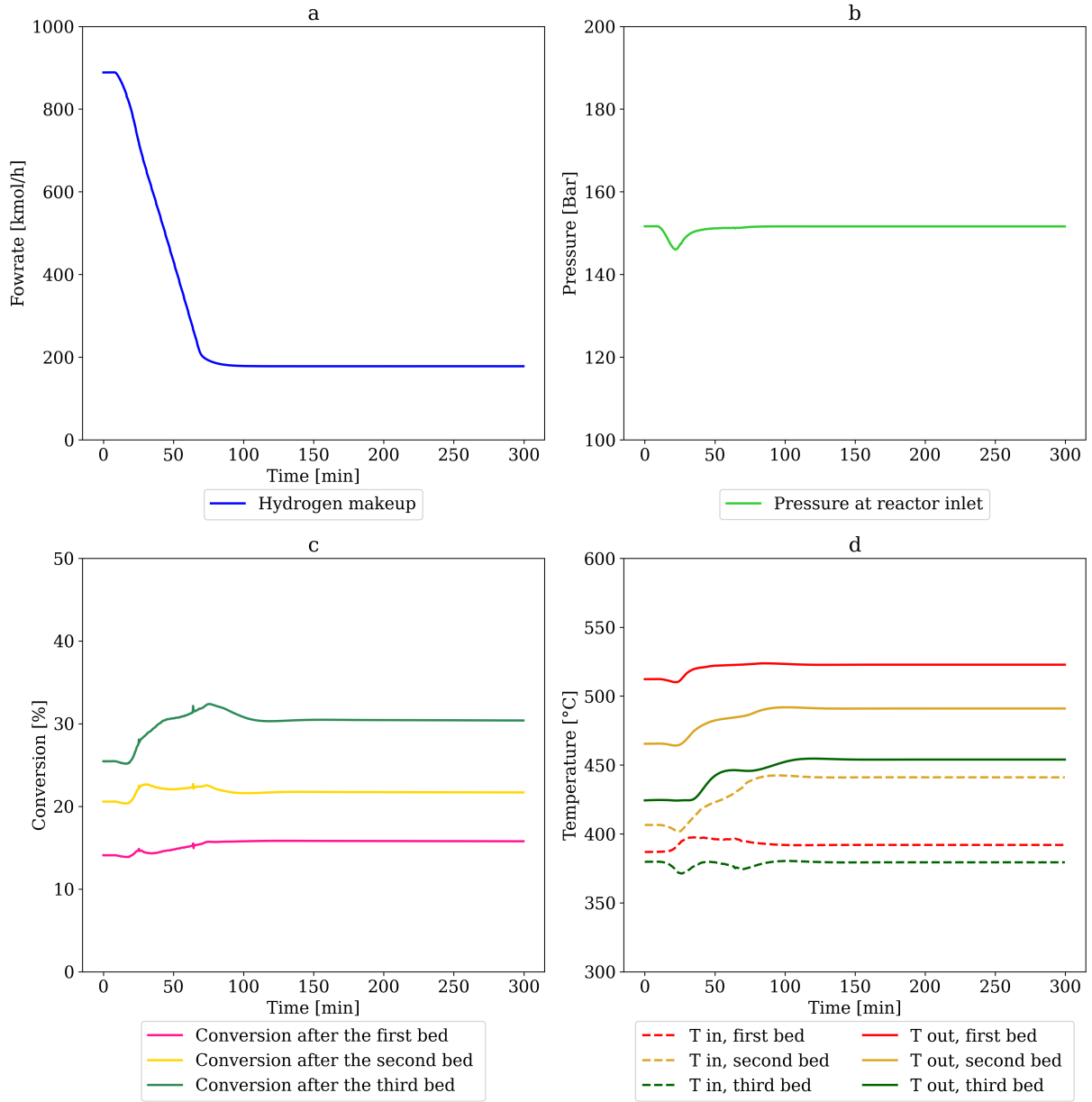


Figure D.6: Results of a decrease of load from 100% to 20% in 60 minutes, using a valve in after the compressor as pressure control

D.2. Stream Tables

D.2.1. Partial Simulation

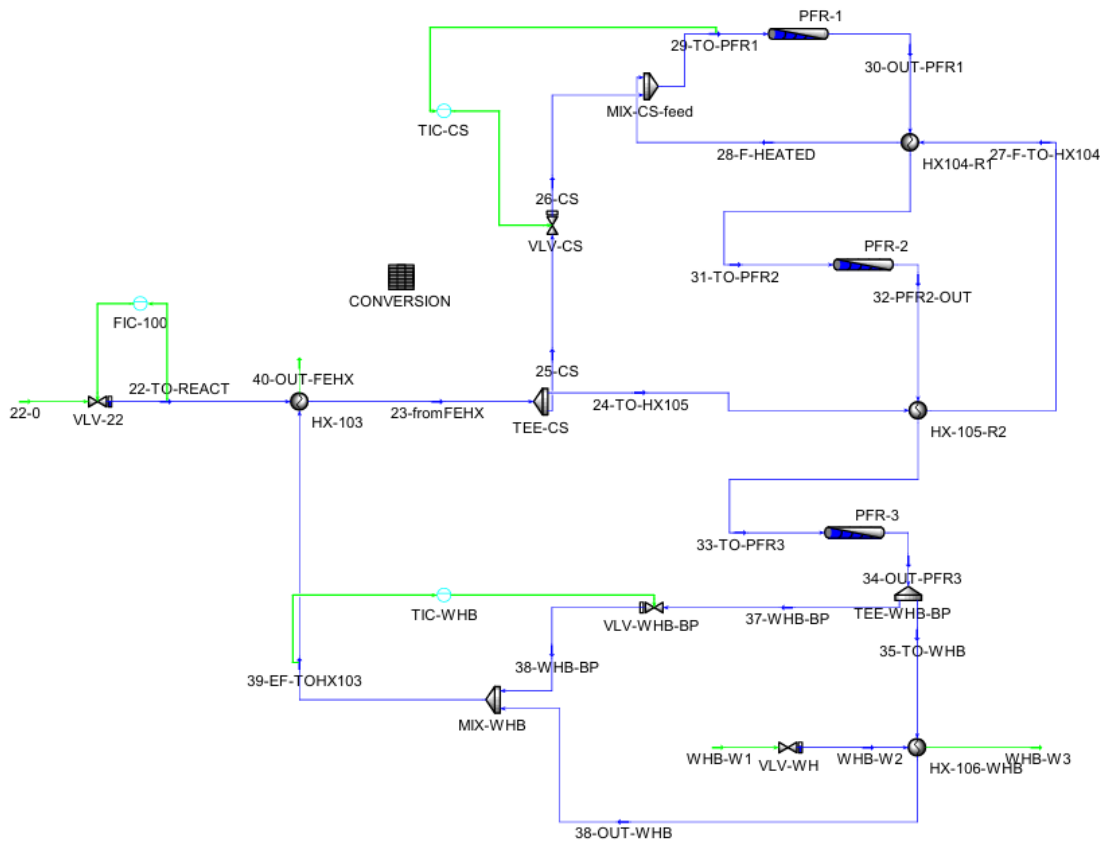


Figure D.7: Partial simulation implemented in UniSim

Table D.1: Stream table, partial simulation, 100% load

	Vap fraction	T [°C]	P [kPa]	kmol/h	kg/h
22-0	1.00	24.57	15220.63	4371.58	39021.19
22-TO-REACT	1.00	24.57	15195.35	4371.58	39021.19
23-fromFEHX	1.00	203.72	15177.34	4371.58	39021.19
24-TO-HX105	1.00	203.72	15177.34	4367.64	38985.97
25-CS	1.00	203.72	15177.34	3.95	35.22
26-CS	1.00	203.73	15096.67	3.95	35.22
27-F-TO-HX104	1.00	289.35	15142.54	4367.64	38985.97
28-F-HEATED	1.00	392.17	15096.67	4367.64	38985.97
29-TO-PFR1	1.00	392.00	15096.67	4371.58	39021.19
30-OUT-PFR1	1.00	515.73	15096.61	4062.51	39021.07
31-TO-PFR2	1.00	412.09	15039.42	4062.51	39021.07
32-PFR2-OUT	1.00	472.91	15039.06	3913.65	39021.00
33-TO-PFR3	1.00	385.76	15005.00	3913.65	39021.00
34-OUT-PFR3	1.00	434.77	15004.67	3795.09	39020.94
35-TO-WHB	1.00	434.77	15004.67	3786.84	38936.13
37-WHB-BP	1.00	434.77	15004.67	8.25	84.80
38-OUT-WHB	1.00	337.79	14968.83	3786.84	38936.13
38-WHB-BP	1.00	434.77	14968.83	8.25	84.80
39-EF-TOHX103	1.00	338.00	14968.83	3795.09	39020.94
40-OUT-FEHX	1.00	148.35	14925.69	3795.09	39020.94
WHB-W1	0.00	99.99	2550.00	2093.95	37722.79
WHB-W2	0.00	100.01	2451.22	2093.95	37722.79
WHB-W3	0.00	172.94	2450.00	2093.95	37722.79

Table D.2: Mole percentage of each component in the streams, partial simulation, 100% load

	H ₂ [%]	N ₂ [%]	NH ₃ [%]	Ar[%]	H ₂ O[%]
22-0	71.99	24.30	3.56	0.15	0.00
22-TO-REACT	71.99	24.30	3.56	0.15	0.00
23-fromFEHX	71.99	24.30	3.56	0.15	0.00
24-TO-HX105	71.99	24.30	3.56	0.15	0.00
25-CS	71.99	24.30	3.56	0.15	0.00
26-CS	71.99	24.30	3.56	0.15	0.00
27-F-TO-HX104	71.99	24.30	3.56	0.15	0.00
28-F-HEATED	71.99	24.30	3.56	0.15	0.00
29-TO-PFR1	71.99	24.30	3.56	0.15	0.00
30-OUT-PFR1	66.05	22.34	11.44	0.17	0.00
31-TO-PFR2	66.05	22.34	11.44	0.17	0.00
32-PFR2-OUT	62.86	21.29	15.67	0.17	0.00
33-TO-PFR3	62.86	21.29	15.67	0.17	0.00
34-OUT-PFR3	60.14	20.40	19.29	0.18	0.00
35-TO-WHB	60.14	20.40	19.29	0.18	0.00
37-WHB-BP	60.14	20.40	19.29	0.18	0.00
38-OUT-WHB	60.14	20.40	19.29	0.18	0.00
38-WHB-BP	60.14	20.40	19.29	0.18	0.00
39-EF-TOHX103	60.14	20.40	19.29	0.18	0.00
40-OUT-FEHX	60.14	20.40	19.29	0.18	0.00
WHB-W1	0.00	0.00	0.00	0.00	100.00
WHB-W2	0.00	0.00	0.00	0.00	100.00
WHB-W3	0.00	0.00	0.00	0.00	100.00

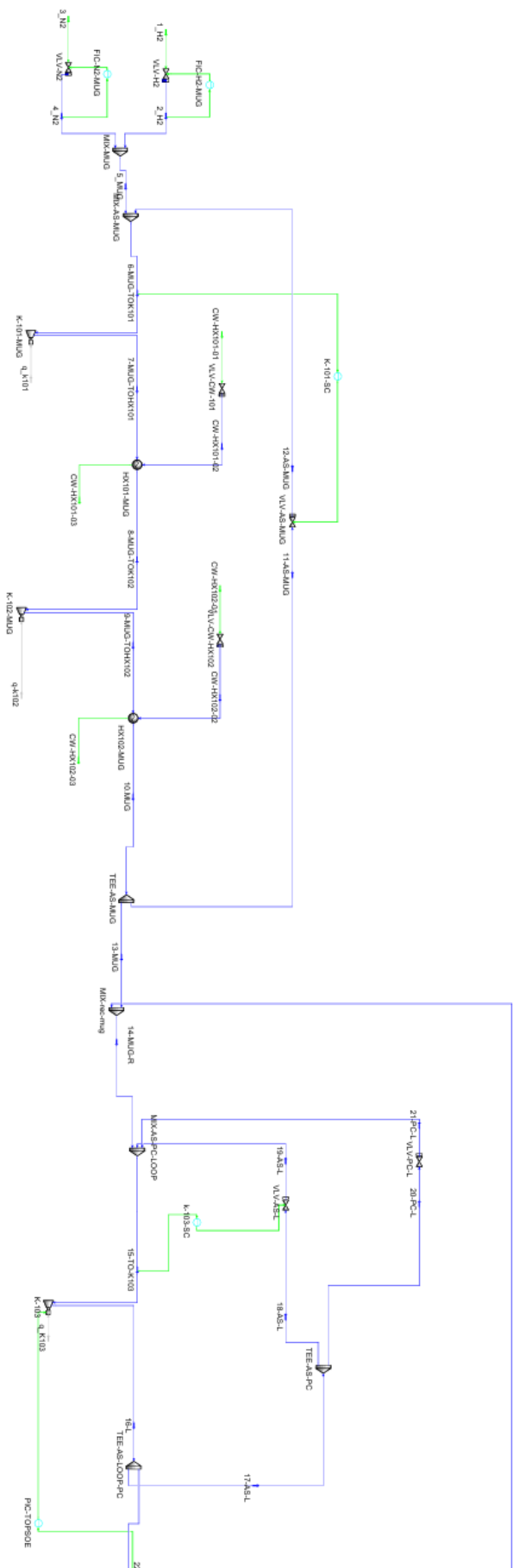
Table D.3: Stream table, partial simulation, 20% load

	Vap fraction	T [°C]	P [kPa]	kmol/h	kg/h
22-0	1.00	24.57	15220.63	874.00	7801.41
22-TO-REACT	1.00	24.50	14936.64	874.00	7801.41
23-fromHX103	1.00	202.60	14935.80	874.00	7801.41
24-TOHX105	1.00	202.60	14935.80	655.62	5852.10
25-CS	1.00	202.60	14935.80	218.38	1949.31
26-CS	1.00	202.60	14933.39	218.38	1949.31
27-F-TO-HX104	1.00	344.26	14934.80	655.62	5852.10
28-F-HEATED	1.00	454.36	14933.39	655.62	5852.10
29-TO-PFR1	1.00	392.00	14933.39	874.00	7801.41
30-OUT-PFR1	1.00	515.11	14933.38	812.51	7801.38
31-TO-PFR2	1.00	431.41	14930.18	812.51	7801.38
32-PFR2-OUT	1.00	483.54	14930.10	786.96	7801.37
33-TO-PFR3	1.00	375.28	14928.21	786.96	7801.37
34-OUT-PFR3	1.00	448.49	14928.14	751.58	7801.35
35-TO-WHB	1.00	448.49	14928.14	302.37	3138.54
37-WHB-BP	1.00	448.49	14928.14	449.22	4662.81
38-OUT-WHB	1.00	170.56	14927.81	302.37	3138.54
38-WHB-BP	1.00	448.49	14927.81	449.22	4662.81
39-EF-TOHX103	1.00	338.00	14927.81	751.58	7801.35
40-OUT-FEHX	1.00	149.01	14925.69	751.58	7801.35
WHB-W1	0.00	99.99	2550.00	2093.88	37721.37
WHB-W2	0.00	100.01	2451.23	2093.88	37721.37
WHB-W3	0.00	117.02	2450.00	2093.88	37721.37

Table D.4: Mole percentage of each component in the streams, partial simulation, 20% load

	H ₂ [%]	N ₂ [%]	NH ₃ [%]	Ar[%]	H ₂ O[%]
22-0	71.99	24.30	3.56	0.15	0.00
22-TO-REACT	71.99	24.30	3.56	0.15	0.00
23-fromHX103	71.99	24.30	3.56	0.15	0.00
24-TOHX105	71.99	24.30	3.56	0.15	0.00
25-CS	71.99	24.30	3.56	0.15	0.00
26-CS	71.99	24.30	3.56	0.15	0.00
27-F-TO-HX104	71.99	24.30	3.56	0.15	0.00
28-F-HEATED	71.99	24.30	3.56	0.15	0.00
29-TO-PFR1	71.99	24.30	3.56	0.15	0.00
30-OUT-PFR1	66.08	22.35	11.39	0.17	0.00
31-TO-PFR2	66.08	22.35	11.39	0.17	0.00
32-PFR2-OUT	63.36	21.46	15.01	0.17	0.00
33-TO-PFR3	63.36	21.46	15.01	0.17	0.00
34-OUT-PFR3	59.28	20.11	20.43	0.18	0.00
35-TO-WHB	59.28	20.11	20.43	0.18	0.00
37-WHB-BP	59.28	20.11	20.43	0.18	0.00
38-OUT-WHB	59.28	20.11	20.43	0.18	0.00
38-WHB-BP	59.28	20.11	20.43	0.18	0.00
39-EF-TOHX103	59.28	20.11	20.43	0.18	0.00
40-OUT-FEHX	59.28	20.11	20.43	0.18	0.00
WHB-W1	0.00	0.00	0.00	0.00	100.00
WHB-W2	0.00	0.00	0.00	0.00	100.00
WHB-W3	0.00	0.00	0.00	0.00	100.00

D.2.2. Complete Simulation, Compressor Speed as the Manipulated Variable for Pressure Control.



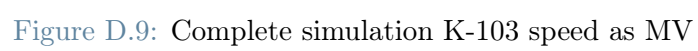


Table D.5: Stream table, complete simulation, 100% load, K103 speed as MV for pressure control

	Vap fraction	T [°C]	P [kPa]	kmol/h	kg/h
1_H2	1.00	25.00	3000.00	888.92	1792.06
2_H2	1.00	25.00	2327.61	888.92	1792.06
3_N2	1.00	25.16	3000.00	296.11	8298.35
4_N2	1.00	23.61	2327.61	296.11	8298.35
5_MUG	1.00	24.12	2327.61	1185.03	10090.40
6-MUG-TOK101	1.00	24.12	2327.61	1185.03	10090.35
7-MUG-TOHX101	1.00	232.10	6648.68	1185.03	10090.35
8-MUG-TOK102	1.00	40.02	6594.74	1185.04	10090.45
9-MUG-TOHX102	1.00	292.39	14842.61	1185.04	10090.45
10.MUG	1.00	30.90	14797.45	1185.05	10090.54
11-AS-MUG	1.00	30.90	14797.45	0.00	0.00
12-AS-MUG	1.00	27.85	2327.61	0.00	0.00
13-MUG	1.00	30.90	14797.45	1185.05	10090.54
14-MUG-R	1.00	6.98	14797.45	4520.71	41956.20
15-TO-K103	1.00	6.99	14797.45	4534.49	42084.14
16-L	1.00	10.86	15182.03	4534.49	42084.14
17-AS-L	1.00	10.86	15182.03	13.79	127.94
18-AS-L	1.00	10.85	15182.03	13.26	123.10
19-AS-L	1.00	10.73	14797.45	13.26	123.10
20-PC-L	1.00	10.85	15182.03	0.52	4.84
21-PC-L	1.00	10.73	14797.45	0.52	4.84
22-TO-REACT	1.00	10.86	15182.03	4520.71	41956.41
23-fromFEHX	1.00	197.86	15163.05	4520.97	41958.59
24-TO-HX105	1.00	197.86	15163.05	4520.97	41958.59
25-CS	1.00	197.86	15163.05	0.00	0.00
26-CS	1.00	198.01	15074.77	0.00	0.00
27-F-TO-HX104	1.00	281.89	15124.98	4521.01	41958.98
28-F-HEATED	1.00	385.22	15074.77	4521.07	41959.48
29-TO-PFR1	1.00	385.22	15074.77	4521.07	41959.48
30-OUT-PFR1	1.00	511.79	15074.71	4193.56	41959.31
31-TO-PFR2	1.00	407.48	15012.29	4193.55	41959.30
32-OUT-PFR2	1.00	466.09	15011.91	4044.99	41958.77
33-TO-PFR3	1.00	380.43	14974.81	4044.99	41958.76

Table D.6: Stream table, complete simulation, 100% load, K103 speed as MV for pressure control, continued

	Vap fraction	T [°C]	P [kPa]	kmol/h	kg/h
34-OUT-PFR3	1.00	425.51	14974.47	3931.84	41957.33
35-TO-WHB	1.00	425.51	14974.47	3425.44	36553.40
36-OUT-WHB	1.00	324.95	14944.09	3425.44	36553.39
37-WHB-BP	1.00	425.51	14974.47	506.41	5403.93
38-WHB-BP	1.00	425.52	14944.09	506.41	5403.93
39-EF-TO-HX103	1.00	338.00	14944.09	3931.84	41957.32
40-OUT-FEHX	1.00	139.78	14897.07	3931.80	41956.89
41-HX107-OUT	0.92	30.41	14843.58	3947.70	42249.07
42-TO-FD	0.85	-1.02	14802.78	3930.91	41942.41
43-TO-SEP	0.85	-1.02	14802.50	3930.14	41929.76
44-FD-0	1.00	-4.32	14797.45	0.00	0.00
44-TO-SEP	0.85	-1.02	14797.63	3930.14	41929.77
44-VFD-0	1.00	-1.02	14800.25	0.00	0.00
45-NH3	0.00	-1.02	14799.34	596.01	10089.55
46-NH3	0.00	0.25	10000.00	596.01	10089.55
47-REC	1.00	-1.02	14796.11	3335.66	31865.68
48-REC	1.00	-1.02	14797.45	3335.66	31865.67
CR-1	0.00	-10.00	1850.00	8617.94	146763.47
CR-2	0.00	-10.00	1840.89	8617.94	146763.47
CR-3	0.00	5.02	1742.71	8617.94	146763.48
CR-4	0.00	4.00	1727.80	-259.17	-4413.64
CR-5	0.00	5.00	1742.72	8877.11	151177.18
CW-HX101-01	0.00	10.00	370.00	5932.67	106877.63
CW-HX101-02	0.00	10.01	317.74	5932.67	106877.63
CW-HX101-03	0.00	24.54	300.00	5932.67	106877.60
CW-HX102-01	0.00	10.00	400.00	5100.20	91880.53
CW-HX102-02	0.00	10.02	312.59	5100.20	91880.53
CW-HX102-03	0.00	33.38	300.00	5100.19	91880.50
CW-HX107-01	0.00	10.00	350.00	14090.79	253847.00
CW-HX107-02	0.00	10.02	269.48	14090.79	253847.00
CW-HX107-03	0.00	27.52	250.00	14090.80	253847.23
WHB-W1	0.00	99.99	2550.00	2093.95	37722.76
WHB-W2	0.00	100.01	2451.22	2093.95	37722.76
WHB-W3	0.00	168.48	2450.00	2093.96	37722.88

Table D.7: Mole percentage of each component in the streams, complete simulation, K103 speed as MV for pressure control, 100% load

	H ₂ [%]	N ₂ [%]	NH ₃ [%]	Ar[%]	H ₂ O[%]
1_H2	100.00	0.00	0.00	0.00	0.00
2_H2	100.00	0.00	0.00	0.00	0.00
3_N2	0.00	99.90	0.00	0.10	0.00
4_N2	0.00	99.90	0.00	0.10	0.00
5_MUG	75.01	24.96	0.00	0.02	0.00
6-MUG-TOK101	75.01	24.96	0.00	0.02	0.00
7-MUG- TOHX101	75.01	24.96	0.00	0.02	0.00
8-MUG-TOK102	75.01	24.96	0.00	0.02	0.00
9-MUG- TOHX102	75.01	24.96	0.00	0.02	0.00
10.MUG	75.01	24.96	0.00	0.02	0.00
11-AS-MUG	75.01	24.96	0.00	0.02	0.00
12-AS-MUG	75.05	24.93	0.00	0.02	0.00
13-MUG	75.01	24.96	0.00	0.02	0.00
14-MUG-R	70.58	25.54	3.69	0.19	0.00
15-TO-K103	70.58	25.54	3.69	0.19	0.00
16-L	70.58	25.54	3.69	0.19	0.00
17-AS-L	70.58	25.54	3.69	0.19	0.00
18-AS-L	70.58	25.54	3.69	0.19	0.00
19-AS-L	70.58	25.54	3.69	0.19	0.00
20-PC-L	70.58	25.54	3.69	0.19	0.00
21-PC-L	70.58	25.54	3.69	0.19	0.00
22-TO-REACT	70.58	25.54	3.69	0.19	0.00
23-fromFEHX	70.58	25.54	3.69	0.19	0.00
24-TO-HX105	70.58	25.54	3.69	0.19	0.00
25-CS	70.58	25.54	3.69	0.19	0.00
26-CS	71.48	24.57	3.77	0.19	0.00
27-F-TO-HX104	70.58	25.54	3.69	0.19	0.00
28-F-HEATED	70.58	25.54	3.69	0.19	0.00
29-TO-PFR1	70.58	25.54	3.69	0.19	0.00
30-OUT-PFR1	64.38	23.63	11.79	0.20	0.00
31-TO-PFR2	64.38	23.63	11.79	0.20	0.00
32-OUT-PFR2	61.23	22.66	15.90	0.21	0.00
33-TO-PFR3	61.23	22.66	15.90	0.21	0.00

Table D.8: Mole percentage of each component in the streams, complete simulation, K103 speed as MV for pressure control, 100% load, continued

	H ₂ [%]	N ₂ [%]	NH ₃ [%]	Ar[%]	H ₂ O[%]
34-OUT-PFR3	58.68	21.87	19.23	0.22	0.00
35-TO-WHB	58.68	21.87	19.23	0.22	0.00
36-OUT-WHB	58.68	21.87	19.23	0.22	0.00
37-WHB-BP	58.68	21.87	19.23	0.22	0.00
38-WHB-BP	58.68	21.87	19.23	0.22	0.00
39-EF-TO-HX103	58.68	21.87	19.23	0.22	0.00
40-OUT-FEHX	58.68	21.87	19.23	0.22	0.00
41-HX107-OUT	58.40	21.77	19.62	0.21	0.00
42-TO-FD	58.69	21.88	19.22	0.22	0.00
43-TO-SEP	58.71	21.88	19.20	0.22	0.00
44-FD-0	71.46	23.85	4.45	0.25	0.00
44-TO-SEP	58.71	21.88	19.20	0.22	0.00
44-VFD-0	69.01	25.74	5.01	0.24	0.00
45-NH3	0.91	0.22	98.82	0.05	0.00
46-NH3	0.91	0.22	98.82	0.05	0.00
47-REC	69.01	25.74	5.01	0.24	0.00
48-REC	69.01	25.74	5.01	0.24	0.00
CR-1	0.00	0.00	100.00	0.00	0.00
CR-2	0.00	0.00	100.00	0.00	0.00
CR-3	0.00	0.00	100.00	0.00	0.00
CR-4	0.00	0.00	100.00	0.00	0.00
CR-5	0.00	0.00	100.00	0.00	0.00
CW-HX101-01	0.00	0.00	0.00	0.00	100.00
CW-HX101-02	0.00	0.00	0.00	0.00	100.00
CW-HX101-03	0.00	0.00	0.00	0.00	100.00
CW-HX102-01	0.00	0.00	0.00	0.00	100.00
CW-HX102-02	0.00	0.00	0.00	0.00	100.00
CW-HX102-03	0.00	0.00	0.00	0.00	100.00
CW-HX107-01	0.00	0.00	0.00	0.00	100.00
CW-HX107-02	0.00	0.00	0.00	0.00	100.00
CW-HX107-03	0.00	0.00	0.00	0.00	100.00
WHB-W1	0.00	0.00	0.00	0.00	100.00
WHB-W2	0.00	0.00	0.00	0.00	100.00
WHB-W3	0.00	0.00	0.00	0.00	100.00

Table D.9: Stream table, complete simulation, 20% load, K103 speed as MV for pressure control

	Vap fraction	T [°C]	P [kPa]	kmol/h	kg/h
1_H2	1.00	25.00	3000.00	177.99	358.83
2_H2	1.00	25.00	2419.83	177.99	358.83
3_N2	1.00	25.16	3000.00	59.29	1661.61
4_N2	1.00	23.83	2419.83	59.29	1661.61
5_MUG	1.00	24.16	2419.83	237.28	2020.44
6-MUG-TOK101	1.00	28.00	2419.83	1211.24	10313.62
7-MUG-TOHX101	1.00	236.16	6837.26	1211.24	10313.62
8-MUG-TOK102	1.00	41.39	6782.20	1211.25	10313.63
9-MUG-TOHX102	1.00	293.60	15215.11	1211.25	10313.63
10.MUG	1.00	31.76	15168.98	1211.25	10313.66
11-AS-MUG	1.00	31.76	15168.98	973.96	8293.18
12-AS-MUG	1.00	28.93	2419.83	973.96	8293.18
13-MUG	1.00	31.76	15168.98	237.29	2020.47
14-MUG-R	1.00	2.11	15168.98	809.68	6971.32
15-TO-K103	1.00	2.45	15168.98	3041.24	26184.99
16-L	1.00	2.58	15182.05	3041.24	26184.99
17-AS-L	1.00	2.58	15182.05	2231.55	19213.63
18-AS-L	1.00	2.58	15182.05	2231.45	19212.76
19-AS-L	1.00	2.58	15168.98	2231.45	19212.74
20-PC-L	1.00	2.58	15182.05	0.10	0.87
21-PC-L	1.00	10.73	15168.98	0.10	0.94
22-TO-REACT	1.00	2.58	15182.05	809.68	6971.37
23-fromFEHX	1.00	194.22	15181.41	809.67	6971.17
24-TO-HX105	1.00	194.22	15181.41	599.59	5162.43
25-CS	1.00	194.22	15181.41	210.08	1808.74
26-CS	1.00	194.22	15179.47	210.08	1808.74
27-F-TO-HX104	1.00	346.32	15180.61	599.59	5162.41
28-F-HEATED	1.00	460.51	15179.47	599.59	5162.35
29-TO-PFR1	1.00	392.00	15179.47	809.67	6971.09
30-OUT-PFR1	1.00	523.06	15179.45	749.50	6970.98
31-TO-PFR2	1.00	437.26	15176.78	749.50	6970.97
32-OUT-PFR2	1.00	489.78	15176.71	725.85	6970.87
33-TO-PFR3	1.00	374.78	15175.13	725.85	6970.85

Table D.10: Stream table, complete simulation, 20% load, K103 speed as MV for pressure control, continued

	Vap fraction	T [°C]	P [kPa]	kmol/h	kg/h
34-OUT-PFR3	1.00	451.91	15175.07	691.62	6970.67
35-TO-WHB	1.00	451.91	15175.07	279.83	2820.36
36-OUT-WHB	1.00	166.99	15174.79	279.83	2820.34
37-WHB-BP	1.00	451.91	15175.07	411.79	4150.31
38-WHB-BP	1.00	451.91	15174.79	411.79	4150.31
39-EF-TO-HX103	1.00	338.00	15174.79	691.62	6970.65
40-OUT-FEHX	1.00	133.49	15173.04	691.62	6970.67
41-HX107-OUT	0.86	12.51	15171.06	691.71	6972.25
42-TO-FD	0.83	-9.74	15169.69	691.71	6971.29
43-TO-SEP	0.83	-9.75	15169.35	691.70	6971.13
44-FD-0	1.00	-4.32	15168.98	0.00	0.00
44-TO-SEP	0.83	-9.74	15169.21	691.70	6971.13
44-VFD-0	1.00	-9.75	15167.19	0.00	0.00
45-NH3	0.00	-9.75	15170.92	119.27	2019.77
46-NH3	0.00	-8.34	10000.00	119.27	2019.77
47-REC	1.00	-9.75	15167.71	572.40	4950.85
48-REC	1.00	-9.74	15168.98	572.40	4950.85
CR-1	0.00	-10.00	1850.00	8580.11	146119.24
CR-2	0.00	-9.99	1840.97	8580.11	146119.24
CR-3	0.00	-8.40	1743.12	8580.11	146119.29
CR-4	0.00	4.00	1727.80	-296.99	-5057.81
CR-5	0.00	-7.98	1743.11	8877.11	151177.18
CW-HX101-01	0.00	10.00	370.00	5933.02	106884.02
CW-HX101-02	0.00	10.01	317.74	5933.02	106884.02
CW-HX101-03	0.00	4.00	1000.00	296.99	5057.81
CW-HX101-04	0.00	10.00	1000.00	296.99	5057.81
CW-HX101-05	0.00	10.00	490.00	5933.02	106884.02
CW-HX101-06	0.00	10.00	1000.00	296.99	5057.81
CW-HX101-07	0.00	10.00	1000.00	296.99	5057.81
CW-HX101-08	0.00	4.00	1000.00	296.99	5057.81

Table D.11: Mole percentage of each component in the streams, complete simulation, K103 speed as MV for pressure control, 20% load

	H ₂ [%]	N ₂ [%]	NH ₃ [%]	Ar[%]	H ₂ O[%]
1_H2	100.00	0.00	0.00	0.00	0.00
2_H2	100.00	0.00	0.00	0.00	0.00
3_N2	0.00	99.90	0.00	0.10	0.00
4_N2	0.00	99.90	0.00	0.10	0.00
5_MUG	75.01	24.96	0.00	0.02	0.00
6-MUG-TOK101	75.01	24.96	0.00	0.02	0.00
7-MUG- TOHX101	75.01	24.96	0.00	0.02	0.00
8-MUG-TOK102	75.01	24.96	0.00	0.02	0.00
9-MUG- TOHX102	75.01	24.96	0.00	0.02	0.00
10.MUG	75.01	24.96	0.00	0.02	0.00
11-AS-MUG	75.01	24.96	0.00	0.02	0.00
12-AS-MUG	75.01	24.96	0.00	0.02	0.00
13-MUG	75.01	24.96	0.00	0.02	0.00
14-MUG-R	73.64	23.64	2.55	0.17	0.00
15-TO-K103	73.64	23.64	2.55	0.17	0.00
16-L	73.64	23.64	2.55	0.17	0.00
17-AS-L	73.64	23.64	2.55	0.17	0.00
18-AS-L	73.64	23.64	2.55	0.17	0.00
19-AS-L	73.64	23.64	2.55	0.17	0.00
20-PC-L	73.64	23.64	2.55	0.17	0.00
21-PC-L	70.58	25.54	3.69	0.19	0.00
22-TO-REACT	73.64	23.64	2.55	0.17	0.00
23-fromFEHX	73.64	23.64	2.55	0.17	0.00
24-TO-HX105	73.64	23.64	2.55	0.17	0.00
25-CS	73.64	23.64	2.55	0.17	0.00
26-CS	73.64	23.64	2.55	0.17	0.00
27-F-TO-HX104	73.64	23.64	2.55	0.17	0.00
28-F-HEATED	73.64	23.64	2.55	0.17	0.00
29-TO-PFR1	73.64	23.64	2.55	0.17	0.00
30-OUT-PFR1	67.51	21.52	10.78	0.19	0.00
31-TO-PFR2	67.51	21.52	10.78	0.19	0.00
32-OUT-PFR2	64.82	20.59	14.39	0.19	0.00
33-TO-PFR3	64.82	20.59	14.39	0.19	0.00

Table D.12: Mole percentage of each component in the streams, complete simulation, K103 speed as MV for pressure control, 20% load, continued

	H ₂ [%]	N ₂ [%]	NH ₃ [%]	Ar[%]	H ₂ O[%]
34-OUT-PFR3	60.61	19.14	20.05	0.20	0.00
35-TO-WHB	60.61	19.14	20.05	0.20	0.00
36-OUT-WHB	60.61	19.14	20.05	0.20	0.00
37-WHB-BP	60.61	19.14	20.05	0.20	0.00
38-WHB-BP	60.61	19.14	20.05	0.20	0.00
39-EF-TO-HX103	60.61	19.14	20.05	0.20	0.00
40-OUT-FEHX	60.61	19.14	20.05	0.20	0.00
41-HX107-OUT	60.60	19.14	20.06	0.20	0.00
42-TO-FD	60.61	19.14	20.05	0.20	0.00
43-TO-SEP	60.61	19.14	20.05	0.20	0.00
44-FD-0	71.46	23.85	4.45	0.25	0.00
44-TO-SEP	60.61	19.14	20.05	0.20	0.00
44-VFD-0	73.07	23.09	3.60	0.24	0.00
45-NH3	0.83	0.17	98.95	0.05	0.00
46-NH3	0.83	0.17	98.95	0.05	0.00
47-REC	73.07	23.09	3.60	0.24	0.00
48-REC	73.07	23.09	3.60	0.24	0.00
CR-1	0.00	0.00	100.00	0.00	0.00
CR-2	0.00	0.00	100.00	0.00	0.00
CR-3	0.00	0.00	100.00	0.00	0.00
CR-4	0.00	0.00	100.00	0.00	0.00
CR-5	0.00	0.00	100.00	0.00	0.00
CW-HX101-01	0.00	0.00	0.00	0.00	100.00
CW-HX101-02	0.00	0.00	0.00	0.00	100.00
CW-HX101-03	0.00	0.00	0.00	0.00	100.00
CW-HX102-01	0.00	0.00	0.00	0.00	100.00
CW-HX102-02	0.00	0.00	0.00	0.00	100.00
CW-HX102-03	0.00	0.00	0.00	0.00	100.00
CW-HX107-01	0.00	0.00	0.00	0.00	100.00
CW-HX107-02	0.00	0.00	0.00	0.00	100.00
CW-HX107-03	0.00	0.00	0.00	0.00	100.00
WHB-W1	0.00	0.00	0.00	0.00	100.00
WHB-W2	0.00	0.00	0.00	0.00	100.00
WHB-W3	0.00	0.00	0.00	0.00	100.00

D.2.3. Complete Simulation, Second Antisurge Line as the Manipulated Variable for Pressure Control.

Table D.13: Stream table, complete simulation, 20% load, second antisurge line as MV for pressure control

	Vap fraction	T [°C]	P [kPa]	kmol/h	kg/h
1_H2	1.00	25.00	3000.00	177.99	358.82
2_H2	1.00	25.00	2419.60	177.99	358.82
3_N2	1.00	25.16	3000.00	59.29	1661.56
4_N2	1.00	23.82	2419.60	59.29	1661.56
5_MUG	1.00	24.16	2419.60	237.27	2020.36
6-MUG-TOK101	1.00	28.03	2419.60	1210.90	10310.72
7-MUG-TOHX101	1.00	236.17	6836.20	1210.90	10310.72
8-MUG-TOK102	1.00	41.36	6781.16	1210.90	10310.72
9-MUG-TOHX102	1.00	293.58	15213.67	1210.90	10310.72
10.MUG	1.00	31.79	15167.57	1210.95	10311.09
11-AS-MUG	1.00	31.79	15167.57	973.63	8290.36
12-AS-MUG	1.00	28.97	2419.60	973.63	8290.36
13-MUG	1.00	31.79	15167.57	237.32	2020.74
14-MUG-R	1.00	2.06	15167.57	813.33	7063.61
15-TO-K103	1.00	5.67	15167.57	32930.62	285990.75
16-L	1.00	5.76	15180.85	32930.62	285990.75
17-AS-L	1.00	5.76	15180.85	32117.30	278927.28
18-AS-L	1.00	5.76	15180.85	0.00	0.00
19-AS-L	1.00	10.78	15167.57	0.00	0.00
20-PC-L	1.00	5.76	15180.85	32117.30	278927.28
21-PC-L	1.00	5.76	15167.57	32117.30	278927.28
22-TO-REACT	1.00	5.76	15180.85	813.33	7063.47
23-fromFEHX	1.00	195.89	15180.19	813.33	7063.44
24-TO-HX105	1.00	195.89	15180.19	599.55	5206.82
25-CS	1.00	195.89	15180.19	213.78	1856.62
26-CS	1.00	195.89	15178.23	213.78	1856.62
27-F-TO-HX104	1.00	347.42	15179.38	599.55	5206.82
28-F-HEATED	1.00	461.14	15178.23	599.55	5206.78
29-TO-PFR1	1.00	392.00	15178.23	813.33	7063.40
30-OUT-PFR1	1.00	523.00	15178.22	752.91	7063.36
31-TO-PFR2	1.00	437.94	15175.49	752.91	7063.35
32-OUT-PFR2	1.00	489.99	15175.42	729.37	7063.32
33-TO-PFR3	1.00	375.97	15173.82	729.37	7063.31

Table D.14: Stream table, complete simulation, 20% load, second antisurge line as MV for pressure control, continued

	Vap fraction	T [°C]	P [kPa]	kmol/h	kg/h
34-OUT-PFR3	1.00	452.36	15173.76	695.28	7063.30
35-TO-WHB	1.00	452.36	15173.76	282.57	2870.58
36-OUT-WHB	1.00	167.60	15173.47	282.57	2870.59
37-WHB-BP	1.00	452.36	15173.76	412.71	4192.71
38-WHB-BP	1.00	452.36	15173.47	412.71	4192.71
39-EF-TO-HX103	1.00	338.01	15173.47	695.28	7063.30
40-OUT-FEHX	1.00	135.23	15171.68	695.28	7063.27
41-HX107-OUT	0.86	12.51	15169.67	695.31	7063.99
42-TO-FD	0.83	-9.74	15168.27	695.32	7063.69
43-TO-SEP	0.83	-9.74	15167.93	695.32	7063.43
44-FD-0	1.00	-4.32	15167.57	0.00	0.00
44-TO-SEP	0.83	-9.74	15167.80	695.32	7063.43
44-VFD-0	1.00	-9.74	15165.75	0.00	0.00
45-NH3	0.00	-9.74	15169.51	119.30	2020.38
46-NH3	0.00	-8.33	10000.00	119.30	2020.38
47-REC	1.00	-9.74	15166.28	576.01	5042.87
48-REC	1.00	-9.74	15167.57	576.01	5042.87
CR-1	0.00	-10.00	1850.00	8580.14	146119.83
CR-2	0.00	-10.00	1840.97	8580.14	146119.83
CR-3	0.00	-8.39	1743.12	8580.14	146119.85
CR-4	0.00	4.00	1727.80	-296.97	-5057.32
CR-5	0.00	-7.97	1743.11	8877.11	151177.18
CW-HX101-01	0.00	10.00	370.00	5933.02	106883.99
CW-HX101-02	0.00	10.01	317.74	5933.02	106883.99
CW-HX101-03	0.00	25.07	300.00	5933.02	106884.01
CW-HX102-01	0.00	10.00	400.00	5100.36	91883.44
CW-HX102-02	0.00	10.02	312.58	5100.36	91883.44
CW-HX102-03	0.00	33.94	300.00	5100.35	91883.30
CW-HX107-01	0.00	10.00	350.00	14069.51	253463.60
CW-HX107-02	0.00	10.02	269.73	14069.51	253463.60
CW-HX107-03	0.00	14.16	250.00	14069.51	253463.65
WHB-W1	0.00	99.99	2550.00	2093.87	37721.34
WHB-W2	0.00	100.01	2451.23	2093.87	37721.34
WHB-W3	0.00	116.26	2450.00	2093.87	37721.36

Table D.15: Mole percentage of each component in the streams, complete simulation, second antsurge line as MV for pressure control, 20% load

	H ₂ [%]	N ₂ [%]	NH ₃ [%]	Ar[%]	H ₂ O[%]
1_H2	100.00	0.00	0.00	0.00	0.00
2_H2	100.00	0.00	0.00	0.00	0.00
3_N2	0.00	99.90	0.00	0.10	0.00
4_N2	0.00	99.90	0.00	0.10	0.00
5_MUG	75.01	24.96	0.00	0.02	0.00
6-MUG-TOK101	75.01	24.96	0.00	0.02	0.00
7-MUG- TOHX101	75.01	24.96	0.00	0.02	0.00
8-MUG-TOK102	75.01	24.96	0.00	0.02	0.00
9-MUG- TOHX102	75.01	24.96	0.00	0.02	0.00
10.MUG	75.01	24.96	0.00	0.02	0.00
11-AS-MUG	75.01	24.96	0.00	0.02	0.00
12-AS-MUG	75.01	24.96	0.00	0.02	0.00
13-MUG	75.01	24.96	0.00	0.02	0.00
14-MUG-R	73.35	23.92	2.56	0.18	0.00
15-TO-K103	73.35	23.92	2.56	0.18	0.00
16-L	73.35	23.92	2.56	0.18	0.00
17-AS-L	73.35	23.92	2.56	0.18	0.00
18-AS-L	73.35	23.92	2.56	0.18	0.00
19-AS-L	70.59	25.52	3.70	0.19	0.00
20-PC-L	73.35	23.92	2.56	0.18	0.00
21-PC-L	73.35	23.92	2.56	0.18	0.00
22-TO-REACT	73.35	23.92	2.56	0.18	0.00
23-fromFEHX	73.35	23.92	2.56	0.18	0.00
24-TO-HX105	73.35	23.92	2.56	0.18	0.00
25-CS	73.35	23.92	2.56	0.18	0.00
26-CS	73.35	23.92	2.56	0.18	0.00
27-F-TO-HX104	73.35	23.92	2.56	0.18	0.00
28-F-HEATED	73.35	23.92	2.56	0.18	0.00
29-TO-PFR1	73.35	23.92	2.56	0.18	0.00
30-OUT-PFR1	67.20	21.83	10.79	0.19	0.00
31-TO-PFR2	67.20	21.83	10.79	0.19	0.00
32-OUT-PFR2	64.53	20.92	14.36	0.20	0.00
33-TO-PFR3	64.53	20.92	14.36	0.20	0.00

Table D.16: Mole percentage of each component in the streams, complete simulation, second antisurge line as MV for pressure control, 20% load, continued

	H ₂ [%]	N ₂ [%]	NH ₃ [%]	Ar[%]	H ₂ O[%]
34-OUT-PFR3	60.34	19.49	19.97	0.21	0.00
35-TO-WHB	60.34	19.49	19.97	0.21	0.00
36-OUT-WHB	60.34	19.49	19.97	0.21	0.00
37-WHB-BP	60.34	19.49	19.97	0.21	0.00
38-WHB-BP	60.34	19.49	19.97	0.21	0.00
39-EF-TO-HX103	60.34	19.49	19.97	0.21	0.00
40-OUT-FEHX	60.34	19.49	19.97	0.21	0.00
41-HX107-OUT	60.33	19.49	19.98	0.21	0.00
42-TO-FD	60.33	19.49	19.97	0.21	0.00
43-TO-SEP	60.34	19.49	19.97	0.21	0.00
44-FD-0	71.46	23.85	4.45	0.25	0.00
44-TO-SEP	60.34	19.49	19.97	0.21	0.00
44-VFD-0	72.66	23.49	3.61	0.24	0.00
45-NH3	0.83	0.17	98.95	0.05	0.00
46-NH3	0.83	0.17	98.95	0.05	0.00
47-REC	72.66	23.49	3.61	0.24	0.00
48-REC	72.66	23.49	3.61	0.24	0.00
CR-1	0.00	0.00	100.00	0.00	0.00
CR-2	0.00	0.00	100.00	0.00	0.00
CR-3	0.00	0.00	100.00	0.00	0.00
CR-4	0.00	0.00	100.00	0.00	0.00
CR-5	0.00	0.00	100.00	0.00	0.00
CW-HX101-01	0.00	0.00	0.00	0.00	100.00
CW-HX101-02	0.00	0.00	0.00	0.00	100.00
CW-HX101-03	0.00	0.00	0.00	0.00	100.00
CW-HX102-01	0.00	0.00	0.00	0.00	100.00
CW-HX102-02	0.00	0.00	0.00	0.00	100.00
CW-HX102-03	0.00	0.00	0.00	0.00	100.00
CW-HX107-01	0.00	0.00	0.00	0.00	100.00
CW-HX107-02	0.00	0.00	0.00	0.00	100.00
CW-HX107-03	0.00	0.00	0.00	0.00	100.00
WHB-W1	0.00	0.00	0.00	0.00	100.00
WHB-W2	0.00	0.00	0.00	0.00	100.00
WHB-W3	0.00	0.00	0.00	0.00	100.00

D.2.4. Complete Simulation, Recycle Valve as the Manipulated Variable for Pressure Control.

Table D.17: Stream table, complete simulation, 20% load, recycle valve as pressure control

	Vap fraction	T [°C]	P [kPa]	kmol/h	kg/h
1_H2	1.00	25.00	3000.00	178.00	358.85
2-H2	1.00	25.00	2350.64	178.00	358.85
3-N2	1.00	25.16	3000.00	59.29	1661.71
4-N2	1.00	23.66	2350.64	59.29	1661.71
5_MUG	1.00	24.13	2350.64	237.30	2020.57
6-MUG-TOK101	1.00	27.16	2350.64	1179.74	10045.36
7-MUG-TOHX101	1.00	235.45	6658.66	1179.74	10045.36
8-MUG-TOK102	1.00	40.20	6605.03	1179.72	10045.24
9-MUG-TOHX102	1.00	292.59	14861.13	1179.72	10045.24
10-MUG	1.00	30.73	14816.41	1179.67	10044.84
11-AS-MUG	1.00	30.74	14816.41	942.44	8024.79
12-AS-MUG	1.00	27.87	2350.64	942.44	8024.79
13-MUG	1.00	30.74	14816.41	237.24	2020.05
14-MUG-R	1.00	1.55	14816.41	824.58	7249.14
15-TOK103	1.00	17.11	14816.41	4214.20	37048.19
16-L	1.00	20.99	15185.91	4214.20	37048.19
17-AS-L	1.00	20.99	15185.91	3389.62	29799.04
18-AS-L	1.00	20.99	15185.91	3389.62	29799.04
19-AS-L	1.00	20.91	14816.41	3389.62	29799.04
20-PC-L	1.00	20.99	15185.91	0.00	0.00
21-PC-L	1.00	26.41	14816.41	0.00	0.00
22-TOREACT	1.00	20.99	15185.91	824.58	7249.15
23-FROMFEHX	1.00	200.90	15185.20	824.55	7248.81
24-TO-HX105	1.00	200.90	15185.20	599.02	5266.15
25-CS	1.00	200.90	15185.20	225.53	1982.66
26-CS	1.00	200.90	15183.21	225.53	1982.66
27-F-TO-HX104	1.00	350.98	15184.37	599.03	5266.14
28-F-HEATED	1.00	463.14	15183.21	599.03	5266.14
29-TO-PFR1	1.00	392.00	15183.21	824.55	7248.80
30-OUT-PFR1	1.00	522.83	15183.19	763.34	7248.70
31-TO-PFR2	1.00	440.37	15180.37	763.35	7248.81
32-PFR2-OUT	1.00	490.76	15180.30	740.19	7248.71
33-TO-PFR3	1.00	379.55	15178.63	740.19	7248.72

Table D.18: Stream table, complete simulation, 20% load, recycle valve as pressure control, continued

	Vap fraction	T [°C]	P [kPa]	kmol/h	kg/h
34-OUT-PFR3	1.00	453.88	15178.56	706.53	7248.54
35-TO-WHB	1.00	453.88	15178.56	291.09	2986.37
36-OUT-WHB	1.00	169.29	15178.26	291.09	2986.36
37-WHB-BP	1.00	453.88	15178.56	415.44	4262.18
38-WHB-BP	1.00	453.88	15178.26	415.44	4262.18
39-EF-TO-HX103	1.00	338.01	15178.26	706.53	7248.54
40-OUT-FEHX	1.00	146.70	15176.44	706.63	7249.59
41-HX107-OUT	0.87	12.63	15174.33	706.69	7250.62
42-TO-FD	0.83	-9.68	15172.87	706.65	7249.74
43-TO-SEP	0.83	-9.69	15172.54	706.64	7249.56
44-FD-0-	1.00	-4.32	15172.17	0.00	0.00
44-TO-SEP	0.83	-9.68	15172.40	706.64	7249.56
44-VFD-0	1.00	-9.69	15170.32	0.00	0.00
45-NH3	0.00	-9.69	15174.10	119.27	2020.04
46-NH3	0.00	-8.28	10000.00	119.27	2020.04
47-REC	1.00	-9.69	15170.86	587.35	5229.13
48-REC	1.00	-9.68	15172.17	587.35	5229.13
49-REC	1.00	-9.82	14816.41	587.35	5229.13
CR-1	0.00	-10.00	1850.00	8232.83	140205.12
CR-2	0.00	-9.99	1836.53	8232.83	140205.12
CR-3	0.00	-8.28	1743.11	8232.83	140205.08
CR-4	0.00	4.00	1727.80	-644.27	-10971.94
CR-5	0.00	-7.38	1743.10	8877.11	151177.18
CW-HX101-01	0.00	9.99	370.00	5932.78	106879.56
CW-HX101-2	0.00	10.01	317.74	5932.78	106879.56
CW-HX101-3	0.00	24.71	300.00	5932.78	106879.66
CW-HX102-01	0.00	9.99	400.00	5100.17	91880.13
CW-HX102-2	0.00	10.02	312.59	5100.17	91880.13
CW-HX102-3	0.00	33.31	300.00	5100.17	91880.08
CW-HX107-1	0.00	10.00	350.00	14069.77	253468.35
CW-HX107-2	0.00	10.02	269.72	14069.77	253468.35
CW-HX107-3	0.00	14.43	250.00	14069.77	253468.37
WHB-W1	0.00	99.99	2550.00	2093.87	37721.36
WHB-W2	0.00	100.01	2451.23	2093.87	37721.36
WHB-W3	0.00	116.72	2450.00	2093.87	37721.30

Table D.19: Mole percentage of each component in the streams, complete simulation, recycle valve as pressure control, 20% load

	H ₂ [%]	N ₂ [%]	NH ₃ [%]	Ar[%]	H ₂ O[%]
1_H2	100.00	0.00	0.00	0.00	0.00
2-H2	100.00	0.00	0.00	0.00	0.00
3-N2	0.00	99.90	0.00	0.10	0.00
4-N2	0.00	99.90	0.00	0.10	0.00
5_MUG	75.01	24.96	0.00	0.02	0.00
6-MUG-TOK101	75.01	24.96	0.00	0.02	0.00
7-MUG- TOHX101	75.01	24.96	0.00	0.02	0.00
8-MUG-TOK102	75.01	24.96	0.00	0.02	0.00
9-MUG- TOHX102	75.01	24.96	0.00	0.02	0.00
10-MUG	75.01	24.96	0.00	0.02	0.00
11-AS-MUG	75.01	24.96	0.00	0.02	0.00
12-AS-MUG	75.01	24.96	0.00	0.02	0.00
13-MUG	75.01	24.96	0.00	0.02	0.00
14-MUG-R	72.93	24.31	2.58	0.18	0.00
15-TOK103	72.93	24.31	2.58	0.18	0.00
16-L	72.93	24.31	2.58	0.18	0.00
17-AS-L	72.93	24.31	2.58	0.18	0.00
18-AS-L	72.93	24.31	2.58	0.18	0.00
19-AS-L	72.93	24.31	2.58	0.18	0.00
20-PC-L	72.93	24.31	2.58	0.18	0.00
21-PC-L	71.97	24.28	3.60	0.16	0.00
22-TOREACT	72.93	24.31	2.58	0.18	0.00
23-FROMFEHX	72.93	24.31	2.58	0.18	0.00
24-TO-HX105	72.93	24.31	2.58	0.18	0.00
25-CS	72.93	24.31	2.58	0.18	0.00
26-CS	72.93	24.31	2.58	0.18	0.00
27-F-TO-HX104	72.93	24.31	2.58	0.18	0.00
28-F-HEATED	72.93	24.31	2.58	0.18	0.00
29-TO-PFR1	72.93	24.31	2.58	0.18	0.00
30-OUT-PFR1	66.75	22.25	10.81	0.19	0.00
31-TO-PFR2	66.75	22.25	10.81	0.19	0.00
32-PFR2-OUT	64.15	21.39	14.27	0.20	0.00
33-TO-PFR3	64.15	21.39	14.27	0.20	0.00

Table D.20: Mole percentage of each component in the streams, complete simulation, recycle valve as pressure control, 20% load

	H ₂ [%]	N ₂ [%]	NH ₃ [%]	Ar[%]	H ₂ O[%]
34-OUT-PFR3	60.06	20.02	19.72	0.21	0.00
35-TO-WHB	60.06	20.02	19.72	0.21	0.00
36-OUT-WHB	60.06	20.02	19.72	0.21	0.00
37-WHB-BP	60.06	20.02	19.72	0.21	0.00
38-WHB-BP	60.06	20.02	19.72	0.21	0.00
39-EF-TO-HX103	60.06	20.02	19.72	0.21	0.00
40-OUT-FEHX	60.06	20.02	19.72	0.21	0.00
41-HX107-OUT	60.05	20.02	19.72	0.21	0.00
42-TO-FD	60.06	20.02	19.72	0.21	0.00
43-TO-SEP	60.06	20.02	19.72	0.21	0.00
44-FD-0-	71.46	23.85	4.45	0.25	0.00
45-NH3	0.82	0.17	98.95	0.05	0.00
46-NH3	0.82	0.17	98.95	0.05	0.00
47-REC	72.09	24.05	3.62	0.24	0.00
48-REC	72.09	24.05	3.62	0.24	0.00
49-REC	72.09	24.05	3.62	0.24	0.00
CR-1	0.00	0.00	100.00	0.00	0.00
CR-2	0.00	0.00	100.00	0.00	0.00
CR-3	0.00	0.00	100.00	0.00	0.00
CR-4	0.00	0.00	100.00	0.00	0.00
CR-5	0.00	0.00	100.00	0.00	0.00
CW-HX101-01	0.00	0.00	0.00	0.00	100.00
CW-HX101-2	0.00	0.00	0.00	0.00	100.00
CW-HX101-3	0.00	0.00	0.00	0.00	100.00
CW-HX102-01	0.00	0.00	0.00	0.00	100.00
CW-HX102-2	0.00	0.00	0.00	0.00	100.00
CW-HX102-3	0.00	0.00	0.00	0.00	100.00
CW-HX107-1	0.00	0.00	0.00	0.00	100.00
CW-HX107-2	0.00	0.00	0.00	0.00	100.00
CW-HX107-3	0.00	0.00	0.00	0.00	100.00
WHB-W1	0.00	0.00	0.00	0.00	100.00
WHB-W2	0.00	0.00	0.00	0.00	100.00
WHB-W3	0.00	0.00	0.00	0.00	100.00

D.2.5. Complete Simulation, Valve after the Compressor as the Manipulated Variable for Pressure Control.

Table D.21: Stream table, complete simulation, 20% load, valve after the compressor as MV for pressure control

	Vap fraction	T [°C]	P [kPa]	kmol/h	kg/h
1_H2	1.0	25.00	3000.0	178.00	358.85
2_H2	1.0	25.00	2421.59	178.00	358.85
3_N2	1.0	25.16	3000.0	59.29	1661.69
4_N2	1.0	23.83	2421.59	59.29	1661.69
5_MUG	1.0	24.16	2421.59	237.30	2020.54
6-MUG-TOK101	1.0	28.01	2421.59	1212.10	10320.87
7-MUG-TOHX101	1.0	236.17	6841.90	1212.10	10320.88
8-MUG-TOK102	1.0	41.42	6786.80	1212.11	10320.98
9-MUG-TOHX102	1.0	293.62	15224.48	1212.11	10320.98
10.MUG	1.0	31.77	15178.32	1212.13	10321.12
11-AS-MUG	1.0	31.77	15178.32	974.80	8300.33
12-AS-MUG	1.0	28.95	2421.59	974.80	8300.33
13-MUG	1.0	31.77	15178.32	237.32	2020.79
14-MUG-R	1.0	1.92	15178.32	824.54	7085.69
15-TO-K103	1.0	17.46	15178.32	4446.90	38215.68
16-L	1.0	21.08	15530.40	4446.90	38215.68
17-AS-L	1.0	21.08	15530.40	3622.36	31129.76
18-AS-L	1.0	21.08	15530.40	3621.58	31123.03
19-AS-L	1.0	21.01	15178.32	3621.58	31122.99
20-PC-L	1.0	21.08	15530.40	0.78	6.73
21-PC-L	1.0	26.41	15178.32	0.78	6.99
22-TO-REACT	1.0	21.08	15530.40	824.54	7085.92
22b	1.0	21.01	15191.63	824.54	7085.91
23-fromFEHX	1.0	200.92	15190.93	824.52	7085.62
24-TO-HX105	1.0	200.93	15190.93	600.23	5158.20
25-CS	1.0	200.93	15190.93	224.28	1927.42
26-CS	1.0	200.93	15188.97	224.28	1927.42
27-F-TO-HX104	1.0	351.22	15190.12	600.23	5158.13
28-F-HEATED	1.0	462.60	15188.97	600.22	5158.08
29-TO-PFR1	1.0	392.00	15188.97	824.51	7085.50
30-OUT-PFR1	1.0	522.95	15188.96	763.28	7085.33
31-TO-PFR2	1.0	440.67	15186.37	763.28	7085.39
32-OUT-PFR2	1.0	490.96	15186.29	740.22	7085.29
33-TO-PFR3	1.0	379.35	15184.66	740.23	7085.30

Table D.22: Stream table, complete simulation, 20% load, valve after the compressor as MV for pressure control, continued

	Vap fraction	T [°C]	P [kPa]	kmol/h	kg/h
34-OUT-PFR3	1.0	453.93	15184.60	706.48	7085.16
35-TO-WHB	1.0	453.93	15184.60	290.75	2915.89
36-OUT-WHB	1.0	168.89	15184.30	290.75	2915.90
37-WHB-BP	1.0	453.93	15184.60	415.73	4169.27
38-WHB-BP	1.0	453.93	15184.30	415.73	4169.27
39-EF-TO-HX103	1.0	338.01	15184.30	706.48	7085.17
40-OUT-FEHX	1.0	146.66	15182.51	706.53	7085.58
41-HX107-OUT	0.87	12.63	15180.45	706.51	7085.39
42-TO-FD	0.83	-9.72	15179.02	706.51	7085.34
43-TO-SEP	0.83	-9.72	15178.68	706.50	7084.92
44-FD-0	1.0	-4.32	15178.32	0.0	0.0
44-TO-SEP	0.83	-9.72	15178.54	706.50	7084.92
44-VFD-0	1.0	-9.72	15176.54	0.0	0.0
45-NH3	0.0	-9.72	15180.26	119.28	2019.92
46-NH3	0.0	-8.31	10000.0	119.28	2019.92
47-REC	1.0	-9.72	15177.05	587.22	5064.90
48-REC	1.0	-9.72	15178.32	587.22	5064.90
CR-1	0.0	-10.0	1850.0	8580.25	146121.72
CR-2	0.0	-10.0	1840.97	8580.25	146121.72
CR-3	0.0	-8.35	1743.12	8580.25	146121.74
CR-4	0.0	4.0	1727.80	-296.87	-5055.62
CR-5	0.0	-7.93	1743.11	8877.11	151177.18
CW-HX101-01	0.0	9.99	370.0	5933.03	106884.14
CW-HX101-02	0.0	10.01	317.74	5933.03	106884.14
CW-HX101-03	0.0	25.08	300.0	5933.03	106884.11
CW-HX102-01	0.0	9.99	400.0	5100.36	91883.54
CW-HX102-02	0.0	10.02	312.58	5100.36	91883.54
CW-HX102-03	0.0	33.96	300.0	5100.37	91883.65
CW-HX107-01	0.0	10.0	350.0	14069.76	253468.22
CW-HX107-02	0.0	10.02	269.72	14069.76	253468.22
CW-HX107-03	0.0	14.43	250.0	14069.77	253468.28
WHB-W1	0.0	99.99	2550.0	2093.87	37721.36
WHB-W2	0.0	100.01	2451.23	2093.87	37721.36
WHB-W3	0.0	116.71	2450.0	2093.88	37721.39

Table D.23: Mole percentage of each component in the streams, complete simulation, valve after the compressor as MV for pressure control, 20% load

	H ₂ [%]	N ₂ [%]	NH ₃ [%]	Ar[%]	H ₂ O[%]
1_H2	100.00	0.00	0.00	0.00	0.00
2_H2	100.00	0.00	0.00	0.00	0.00
3_N2	0.00	99.90	0.00	0.10	0.00
4_N2	0.00	99.90	0.00	0.10	0.00
5_MUG	75.01	24.96	0.00	0.00	0.00
6-MUG-TOK101	75.01	24.96	0.00	0.00	0.00
7-MUG- TOHX101	75.01	24.96	0.00	0.00	0.00
8-MUG-TOK102	75.01	24.96	0.00	0.00	0.00
9-MUG- TOHX102	75.01	24.96	0.00	0.00	0.00
10.MUG	75.01	24.96	0.00	0.00	0.00
11-AS-MUG	75.01	24.96	0.00	0.00	0.00
12-AS-MUG	75.01	24.96	0.00	0.00	0.00
13-MUG	75.01	24.96	0.00	0.00	0.00
14-MUG-R	73.69	23.56	2.57	0.18	0.00
15-TO-K103	73.69	23.56	2.57	0.18	0.00
16-L	73.69	23.56	2.57	0.18	0.00
17-AS-L	73.69	23.56	2.57	0.18	0.00
18-AS-L	73.69	23.56	2.57	0.18	0.00
19-AS-L	73.69	23.56	2.57	0.18	0.00
20-PC-L	73.69	23.56	2.57	0.18	0.00
21-PC-L	71.97	24.28	3.60	0.16	0.00
22-TO-REACT	73.69	23.56	2.57	0.18	0.00
22b	73.69	23.56	2.57	0.18	0.00
23-fromFEHX	73.69	23.56	2.57	0.18	0.00
24-TO-HX105	73.69	23.56	2.57	0.18	0.00
25-CS	73.69	23.56	2.57	0.18	0.00
26-CS	73.69	23.56	2.57	0.18	0.00
27-F-TO-HX104	73.69	23.56	2.57	0.18	0.00
28-F-HEATED	73.69	23.56	2.57	0.18	0.00
29-TO-PFR1	73.69	23.56	2.57	0.18	0.00
30-OUT-PFR1	67.57	21.44	10.80	0.19	0.00
31-TO-PFR2	67.57	21.44	10.80	0.19	0.00
32-OUT-PFR2	65.01	20.55	14.25	0.20	0.00
33-TO-PFR3	65.01	20.55	14.25	0.20	0.00

Table D.24: Mole percentage of each component in the streams, complete simulation, valve after the compressor as MV for pressure control, 20% load, continued

	H ₂ [%]	N ₂ [%]	NH ₃ [%]	Ar[%]	H ₂ O[%]
34-OUT-PFR3	60.95	19.14	19.70	0.20	0.00
35-TO-WHB	60.95	19.14	19.70	0.20	0.00
36-OUT-WHB	60.95	19.14	19.70	0.20	0.00
37-WHB-BP	60.95	19.14	19.70	0.20	0.00
38-WHB-BP	60.95	19.14	19.70	0.20	0.00
39-EF-TO-HX103	60.95	19.14	19.70	0.20	0.00
40-OUT-FEHX	60.95	19.14	19.70	0.20	0.00
41-HX107-OUT	60.95	19.14	19.70	0.20	0.00
42-TO-FD	60.95	19.14	19.70	0.20	0.00
43-TO-SEP	60.95	19.14	19.70	0.20	0.00
44-FD-0	71.46	23.85	4.45	0.25	0.00
44-TO-SEP	60.95	19.14	19.70	0.20	0.00
44-VFD-0	73.16	22.99	3.61	0.24	0.00
45-NH3	0.84	0.17	98.95	0.05	0.00
46-NH3	0.84	0.17	98.95	0.05	0.00
47-REC	73.16	22.99	3.61	0.24	0.00
48-REC	73.16	22.99	3.61	0.24	0.00
CR-1	0.00	0.00	100.00	0.00	0.00
CR-2	0.00	0.00	100.00	0.00	0.00
CR-3	0.00	0.00	100.00	0.00	0.00
CR-4	0.00	0.00	100.00	0.00	0.00
CR-5	0.00	0.00	100.00	0.00	0.00
CW-HX101-01	0.00	0.00	0.00	0.00	100.00
CW-HX101-02	0.00	0.00	0.00	0.00	100.00
CW-HX101-03	0.00	0.00	0.00	0.00	100.00
CW-HX102-01	0.00	0.00	0.00	0.00	100.00
CW-HX102-02	0.00	0.00	0.00	0.00	100.00
CW-HX102-03	0.00	0.00	0.00	0.00	100.00
CW-HX107-01	0.00	0.00	0.00	0.00	100.00
CW-HX107-02	0.00	0.00	0.00	0.00	100.00
CW-HX107-03	0.00	0.00	0.00	0.00	100.00
WHB-W1	0.00	0.00	0.00	0.00	100.00
WHB-W2	0.00	0.00	0.00	0.00	100.00
WHB-W3	0.00	0.00	0.00	0.00	100.00

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List of Symbols

Variable	Description	SI unit
α	Kinetic parameter	-
γ	Kinetic parameter	-
ΔP	Pressure difference	Pa
ΔT	Temperature difference	K
ΔT_{ml}	logarithmic mean temperature difference	K
η	Effectiveness factor	-
Θ	Delay	s
ρ	Density	kg/m ³
τ	Process time constant	s
τ_2	Second order process time constant	s
τ_D	Derivate time	s
τ_I	Integral time	s

Variable	Description	SI unit
A	Area	m^2
a_i	Activity of species i	Pa
cv	Valve conductance	$\text{kg/s}/(\text{Pa kg/m}^3)^{0.5}$
D	Diameter	m
e	Error function	s
k	Process gain	
K_C	Controller gain	
k_{eq}	Equilibrium constant	s
k_i	Kinetic constant	s
$\dot{m}$	Mass Flow	kg/s
p_i	Partial pressure of i	Pa
Q	Duty	W
r	Reaction rate	$\text{mol/m}^3/\text{s}$
U	Heat transfer coefficient	$\text{W/m}^2/\text{K}$
u	Manipulated variable	
V	Volume	m^3
$\dot{V}$	Volumetric Flow	m^3/s
y	Process variable	
y_s	Process variable set point	

Acronyms

ASU	Air Separation Unit
EU	European Union
FEHE	Feed Effluent Heat Exchanger
HX	Heat Exchanger
K	Compressor
MUG	Makeup gas
NTNU	Norwegian University of Science and Technology
PEM	Polimeric Electrolyte Membrane
PFD	Process Flow Diagram
PFR	Plug Flow Reactor
PID	Proportional, Integral, Deivate
POLIMI	Politecnico di Milano
PSA	Pressure Swing Adsorption
RDS	Rate Determining Step
TEMA	Tubular Exchanger Manufacturer Association
WHB	Waste Heat Boiler

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