NTNU – Trondheim
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Optimisation of an Ammonia Synthesis Loop

Investigation of a Novel Approach for Optimisation of Integrated plants

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Abstract

A Hysys model representing the steady state behaviour of a Haber-Bosch ammonia plant was developed based on a dynamic model and plant data from Norwegian fertiliser company Yara International ASA. The plant model was optimised using MATLABs `fmincon` function with an interior-point method for economical optimisation with the aim to study the performance of different strategies.

The Haber-Bosch ammonia plant represents an interconnected complex system with many nested mass and energy streams that make for a challenging optimisation. Therefore this thesis studies the effect of separating the plant model into units that are optimised separately to reduce the computational effort needed for the optimisation. These units consists of the synthesis gas makeup, reaction, separation and refrigeration sections.

Two strategies where proposed, one were the plant refrigeration section was separated out from the plant model, which greatly reduced the amount of nested loops in the problem. The 2nd strategy replaced the separation and refrigeration section of the plant with a simplified model in the first optimisation set. The individual sections of both strategies were independently optimised

There were several difficulties with developing a model that allowed for a wide range of operating configurations of the ammonia plant in Hysys. In addition a few unphysical aspects of the Hysys model were uncovered, such as the compressor lacking an upstream flow effect and poor methods for evaluating pressure drop for varying conditions. These challenges meant that the optimisation problem was only posed for a limited window of operation for the process. Thus, for application to a real world plant the results should be scrutinised.

The optimisation strategies were successful in improving the plant profitability from the nominal operating point. In addition, as expected, the division decreased the computational effort needed for each optimisation. Further work is required to develop the separation strategy and identify possible limitations.

Sammendrag

En HYSYS modell som representer den stasjonære tilstanden for en ammoniakkfabrikk basert på Haber-Bosch prosessen ble utledet basert på anleggsdata og en dynamisk modell fra den norske gjødselprodusenten Yara International ASA. Hensikten med dette var å uføre en økonomisk optimalisering av anleggsdriften ved bruk av MATLABs funksjon `fmincon` med en "interior-point" optimaliseringsmetode for å vurdere ulike optimaliseringsstrategier.

Haber-Bosch-prosessen utgjør en tett koblet og kompleks prosess med flere resirkulasjonsstrømmer og nøstede løkker for varmeintegrasjon. Denne sammenkoblingen gir en utfordrende optimalisering og studien så på ulike optimaliseringsstrategier for å forenkle optimaliseringsproblemet. Konseptet var å studere anlegget i ulike deler og å optimalisere sett av enhetene hver for seg. Disse enhetene er klargjøring av syntesegassen, reaktor-, separasjon- og kjøleseksjonene. Ideen med å partisjonene anlegget er å redusere beregningsbehovet for å finne en optimal løsning for driften av anlegget.

To separasjonsstrategier ble foreslått, én der kjøleseksjonen ble separert ut og optimalisert som en egen enhet. Dette reduserer antallet nøstede løkker i HYSYS-flytskjemaet betraktelig. Den andre strategien erstattet separasjon- og kjøleseksjonen med en forenklet modell og optimaliserte syntesegass og reaktor seksjonen med den forenklede modellen, mens separasjon- og kjøleseksjonen ble optimalisert som et sett.

Det viste seg å være vanskelig å utvikle en stasjonær modell i HYSYS som representerte prosessen på en fysikalsk korrekt måte for et bredt spekter av prosessbetingelser. Svakheter knyttet til modelleringen av den stasjonære tilstanden i HYSYS ble også avdekket, som manglende oppstrøms effekt fra kompressorer og svake metoder for å vurdere trykkfallet over prosessenheter, spesielt varmevekslere. Dette resulterte i at prosessen kun ble optimalisert for et begrenset vindu av prosessbetingelser og at resultatene må vurderes nøye for applikasjon på et virkelig anlegg.

Optimaliseringsstrategien var vellykket med tanke på å øke anleggsinntektene for de gitte prosessbetingelsene og som forventet ble beregningsbehovet redusert for hver optimalisering. Mer arbeid er nødvendig for å utvikle separasjonsstrategien og for å identifisere mulige begrensninger med denne.

Acknowledgements

This thesis has been written as the conclusion of the M.Sc degree in Chemical Engineering from the Norwegian University of Science and Technology. The work has been completed at the group for Process Systems Engineering.

I would like to thank my main supervisor, Sigurd Skogestad, for the possibility to write this thesis on an interesting and challenging subject at his research group, where the academic level and technical skill of the staff has only grown more impressive with the time spent here. I am forever grateful for the knowledge that has been instilled in me through lectures and working with the professors, PhD-candidates and fellow students on the 2nd floor of Chemistry Block IV.

This whole project would not have been possible without the guidance and motivation from PhD-candidate Julian Straus, my co-supervisor. I hope that this work will prove to be of benefit for your doctoral work and I cannot express my gratitude enough for the effort you have spent with me.

These five years of studies have been made into student life with the company and support from my friends and family, I look forward to future adventures!

Statement of Compliance

I declare that this is an independent work according to the exam regulations of the Norwegian University of Science and Technology (NTNU).

Trondheim, 18th June 2015

Martin Jonathan Bland

Contents

Chapter 1

Introduction

For this master thesis an ammonia-plant has been investigated with regards to optimal operation. This study also looks into strategies for optimisation of large scale interconnected plants, such as the Haber-Bosch process for ammonia production. Optimality for a chemical plant in this context is to produce the maximum or desired amount of product for the lowest achievable cost whilst satisfying constraints like product specifications and environmental limits. The plant studied is operated by the Norwegian company Yara, a major global fertiliser manufacturer and the worlds largest producer of ammonia.

1.1 Ammonia

Ammonia, NH_3, is the 2nd most manufactured industrial chemical in the world per weight. 80% of the annual production of 160 Mtons NH_3 is applied as fertiliser either directly or as other ammonium based products [13]. Ammonia is also used for a wide range of applications such as a feedstock for textiles, chemical products and explosives. Most modern NH_3-plants use the Haber-Bosch process to produce ammonia from nitrogen and hydrogen obtained from air and (mainly) natural gas. These processes are operated with reactor temperatures of 400-500°C and pressures ranging from 100-200 bar with considerable recycle of uncreated synthesis gas [1]. The exothermic reaction and high reactor operating temperature means that there is a large potential for energy integration of the process to minimise the use of external energy utilities. This interconnectedness of ammonia plants adds complexity resulting in a challenging optimisation, where changing a process variable may have a hard to predict impact over the whole plant.

The huge scale and global knowledge of the Haber-Bosch process implies that the production process has to be optimal in order to remain competitive in a global and established yet fluctuating market. Estimates indicate that the global production capacity of ammonia will increase by more than 15% from 2015 to 2018, possibly lowering the price of ammonia if the demand does not simultaneously grow at the same rate [13]. On the other hand decreasing oil and gas prices may for example also result in cheaper synthesis gas make up and plant utilities. Thus, optimisation and ensuing control must take into account changing conditions, such as changes in product price or utilities during the plants operation horizon.

1.2 Modelling and optimisation

The basis for optimisation is the mathematical representation of the studied process. Commercial modular process simulators, such as HYSYS®, provide a tool for defining a flowsheet model for large scale systems from a library of unit operations. For example reactors or compressors allow the development and simulation of a huge variety of different process flow diagrams (PFDs).

Optimisation methods suited for application in this kind of modular flowsheets have been developed to the point where they can handle large scale problems and converge these to an optimal solution [16]. However using the full scale model defined in the modular simulator for the optimisation may be computationally expensive. Especially phase composition calculations in the refrigeration section of an ammonia plant are demanding but unnecessary for the potential objective function of the optimisation. Hence this thesis will look into the effect of separating and simplifying the plant model for a more effective optimisation.

1.3 Scope of work

The objective of this thesis is to develop a steady state model of a NH_3 based on data and a dynamic model of a plant operated by Yara. This model is used to study the effect of separated and simplified plant models on the performance of the process optimisation.

1.4 Structure of the thesis

This report consists of 7 chapters and 5 appendices

Chapter 1. Gives a brief introduction to the study and motivation for the ammonia process optimisation.

Chapter 2. Introduces the basis NH_3 process chemistry and describes the studied plant.

Chapter 3. Details the modelling done for the Yara plant in HYSYS.

Chapter 4. Defines the optimisation problem and the mathematical formulation for the optimisation function.

Chapter 5. Presents the results of the optimisation.

Chapter 6. Contains the discussion and what could be done in further work.

Chapter 7. Is the final conclusion

Appendices Contain a brief description of the upstream syngas preparation and the key disturbances that may origin here, the initial process conditions, a description of the turbines and an example of the software framework for the optimisation.

Chapter 2

Ammonia Production

This following section gives an overview of the history of the Haber-Bosch process and describes the main aspects of the chemistry for Haber-Bosch ammonia production and the configuration of the plant operated by Yara.

2.1 History of ammonia production

The need for NH_3-production from abundantly available resources, such as air and natural gas, came about from the vast population growth following in the wake of the industrial revolution in the 1800s. More mouths to feed demanded increased agricultural output and the answer to this was the large scale application of fertilisers [19]. One of the main nutrients in all fertilisers are fixated nitrogen[1] together with phosphor and potassium. Early nitrogen sources were bird manure or nitrate salts found in the deserts of West coast South-America. However these resources were too remote and limited to match the growing demand in the 1800s. Also the long transport distances were vulnerable to blockade and politics influencing the supply of crucial resources.

This increasing demand for fixated nitrogen motivated the development of novel chemical processes which was extensively investigated in the late 1800s. The first production of NH_3 was as a by-product from destructive distillation of coal as NH_4OH. One of the 1st primary production methods for nitrogen fixation with air as the N_2-source was the Frank-Caro or

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[1] N_2 converted to species where it may be used as nutrient, such as ${NH_4}^+$ or ${NO_3}^-$

Cyanamide-process which reacted nitrogen with calcium carbide. However these methods produced fixated nitrogen with too limited quality and output to match demand (and were eventually outcompeted by the more effective Haber-Bosch process). Therefore the development of the Haber-Bosch process by Fritz Haber and Carl Bosch for producing NH_3 from hydrogen and atmospherical nitrogen was a breakthrough technological development that enabled the wast continued population growth in the 1900s.

The main challenge faced in developing the Haber-Bosch process was to build a reaction scheme that proceeded with an acceptable rate and yield at feasible process conditions. Haber and Robert Le Rossignol developed an iron based catalyst and investigated the reaction conditions which showed promise for application as an industrial process. Bosch industrialised the process for BASF by developing large capacity high pressure and temperature equipment. Fritz Haber was awarded the Nobel prize in 1918 for the discovery of ammonia production from hydrogen and nitrogen. The Haber-Bosch process was also one of the first steps into high pressure process chemistry and Bosch received the Nobel prize in 1931 for his contributions to high pressure chemistry working on the Haber-Bosch, Fischer-Tropsch and methanol synthesis processes.

In Norway the Birkeland-Eyde process using electrical arcs to produce nitric acid, HNO_3, from air was developed and industrialised in 1905. However, compared to the Haber-Bosch process, the arc process is very energy inefficient and Norwegian nitrogen fixation was shifted to the Haber-Bosch process and NH_3-production by 1924.

2.2 Process chemistry

The exothermic reaction to produce NH_3 from N_2 and H_2 proceeds by the following reaction:

$$\mathrm{N_2 + 3H_2 \rightleftharpoons 2NH_3} \quad \Delta \mathrm{H}^\circ_{\mathrm{rx}} = -91.8\ \mathrm{kJ/mol} \tag{2.1}$$

Equilibrium studies show that low temperatures and high pressures are preferred for large degree of conversion to NH_3 which can be seen as a practical example of Le Chateliers principle [17][18]. However due to the very strong covalent triple bond of N_2 a high activation energy is required to separate N_2 to its activated state for the reaction to proceed. This means that at thermodynamically favourable conditions (large degree of conversion to ammonia of the reactants) the reaction proceeds too slowly to be acceptable at an industrial scale[2]. Alternative processes provide the required activation energy via electrical or ionizing radiation (plasma processes), directly reacting the nitrogen with oxygen and then water to produce nitric acid avoiding the unfavourable equilibrium reaction. Nonetheless these processes are inefficient, as a considerable amount of energy is lost to heat and incidental radiation, compared to Haber-Bosch.

To achieve measurable reaction rates temperatures above 1200 K are required, but this results in a very low yield. For pressures above 2000 bar the reaction proceeds without a specific catalyst and appears to be catalysed by the reactor walls. However these conditions are to harsh for application in an industrial plant; therefore all Haber-Bosch NH_3-plants utilise catalysts to lower the required reaction activation energy. Thus reducing the reactor operating temperature resulting in more favourable conditions for NH_3 production. Pressure also has a large impact on the reaction rate together with temperature. Higher pressures raises the reaction rate as the activity of the reacting species rises, as can be seen from the model rate expression in Equation 3.7 on page 20. In addition elevated pressures increases the equilibrium conversion of NH_3. However one cannot increase the pressure indefinitely and it is limited by equipment capabilities and compressor investment and operating costs. Typical reactor temperatures and pressures for the Haber-Bosch process are 400-500°C and 100-150 bar. The pressure drop over the reactor is determined by the flow and properties of the catalyst in the reactor bed, which is briefly mentioned in the description of the reactor modelling, Section 3.2.5.

The catalysts used for the Haber-Bosch are mainly self-supported iron-based catalysts promoted with elements such as calcium, potassium and aluminium. They operate in a temperature range from 250-500°C. At higher reaction temperatures the catalyst deactivation rate increases due to acceleration of structural changes and oxidation (the maximum recommended reactor temperature is typically 530°C). This shortens the catalyst lifespan below practicable limits for a continuous plant application. At lower temperatures the reaction rate drops, the reaction extinguishes and the recirculation rate of unreacted synthesis gas, syngas, becomes excessive for the process equipment. If the reactor is operated properly with adequate removal of catalyst poisons and not exceeding the temperature limits, running times without catalyst replacement exceeding 14 years are achievable.

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[2] Reactor sizes would be excessive or even infeasible for low temperature-high conversion NH_3 production

The reactor configuration, especially with regards to temperature control, is key to achieving a sustained catalyst life. It is desirable to operate at a high temperature with fast reaction whilst still staying below the temperature constraint. The reactor type studied in this thesis achieves this by operating two adiabatic reactor beds (albeit with some heat loss trough the reactor jacket) with quenching by feed syngas at both bed outlets. Figure B.1 in Appendix B.2 illustrates the nominal reactor profile. The catalyst oxidation at elevated temperatures is caused by oxygen containing components such as H_2O and CO which reversibly oxidises the catalyst. These are inherently present in the syngas due to the steam reforming reactions used for feed preparation. Other more severe catalyst poisons include sulphur, phosphor, arsenic and chlorine containing compounds. These are typically removed upstream of the syngas production as they also poison these processes. With regards to economical optimisation it is important to note that syngas prepration of H_2 and N_2 from water and air is the largest contributor to the plant operating cost. On a weight basis the syngas cost is roughly 2/3 of the NH_3 value (see Table 4.1 for all relative utility costs). Thus, reducing the syngas cost has a major effect on the production profitability. Also developing catalysts that allow for an acceptable reaction rate at lower reactor operating temperatures gives a higher degree of conversion to NH_3 and lower operating costs. These aspects of operation development is related to process development and beyond the scope of this thesis. Further details on the NH_3-synthesis thermodynamics, kinetics, catalysis and reactor are given in Chapters 3-6 of [1].

2.3 Plant description

The plant studied is a single train plant that can be viewed as four interconnected subunits as shown in the block diagram in Figure 2.1. In the following description the main components, cost contributors and constraints are described in each plant section. The constraints are given for the physical limitations in the plant.

The raw material for the process is syngas consisting of N_2 and H_2 in a molar ratio of 3:1. There are also impurities consisting of helium, argon, water, methane and carbon dioxide. Syngas preparation is discussed in Appendix A, with plant nominal conditions in the various sections presented in Appendix B.

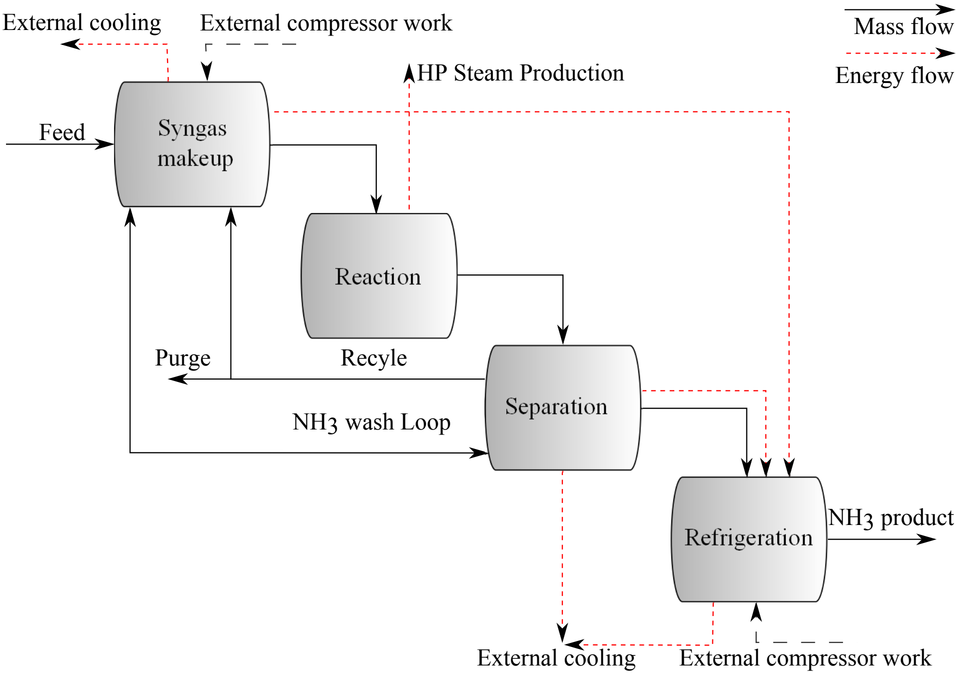

Figure 2.1: Block diagram of main processes in a NH_3-plant, based on the design of a Yara operated plant.

2.3.1 Syngas makeup

The syngas make up section compresses the fresh syngas and washes it with liquid ammonia to remove any water from the feed, before the fresh and recycled syngas is compressed to the reaction section operating pressure. The process flow diagram (PFD) for the syngas makeup section is presented in Figure 2.2.

Process description

The incoming syngas is compressed in a back pressure compressor (C1-BP) to match the NH_3-wash loop pressure. After compression the syngas is cooled over two heat exchangers with cooling water (CW-1) and ammonia (HEX-1) from the refrigeration section. Any condensed water is removed by separation tank S-1. Remaining water and carbon dioxide in the syngas oxidises the catalyst and has to be removed which is achieved by washing the syngas stream with liquid ammonia from the outlet of the separation section. The manipulated valve VLV-1 controls the flow of ammonia in

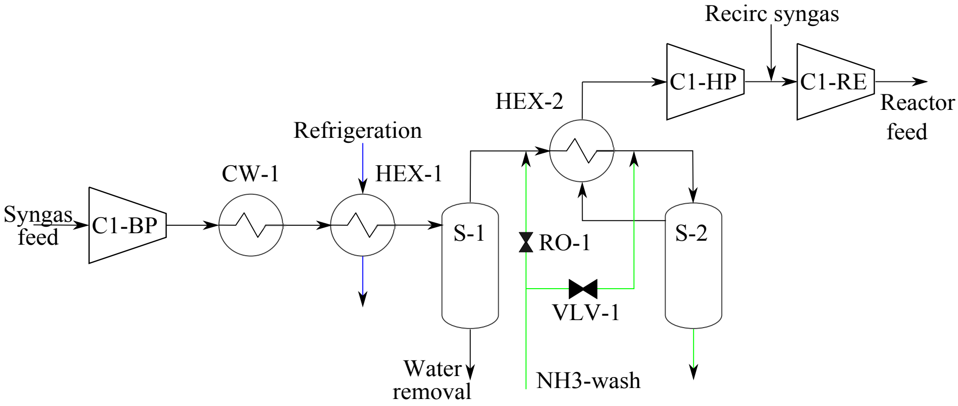

Figure 2.2: PFD for the syngas makeup section in the NH_3-plant.

to the section whilst the pressure drop over the relief orifice RO-1 vaporises most of the liquid ammonia that passes through HEX-2. The gaseous syngas/NH_3 stream is cooled to a two phase stream by HEX-2 and further addition of liquid NH_3. The stream is split by separator S-2 with the water and carbon dioxide being dissolved in the polar ammonia and removed in the liquid stream together with most of the NH_3 and some dissolved gases. The dried syngas is then cross heated by HEX-2, before it is compressed by the high pressure compressor C1-HP to the outlet pressure of the separation section. The heating and cooling in HEX-2 is a clear example of heat integration in the plant. Finally, the fresh syngas is mixed with the recycle and compressed to the reaction section operating pressure by compressor C1-RE.

It is important to note that all three compressors in the syngas make-up section are connected on a single drive shaft and powered by the same turbine. This means that the pressure at the compressor outlet can not be independently set. In the current configuration of the plant the shaft speed is used for flow control of the fresh feed rate. Further details on the compressor and turbine are given in Appendix C.

Cost contributors

The direct cost contributors to the process in this section are the syngas, compressor operating and cooling utility costs. More cooling over the heat exchangers increases the compressor efficiency, but also the utility cost (both cooling water and refrigeration). The ammonia wash stream has two effects on the plant operating cost; firstly it gives a larger syngas flow which raises the required compressor work and and secondly ammonia in reactor feed stream decreases the conversion to ammonia in the reactors due to the equilibrium reaction. The flow rate of the wash stream should there be kept as low as possible whilst still ensuring proper water removal.

Constraints

The following constraints have been identified for the syngas makeup section:

- Maximum H_2O content in the fresh syngas feed is 5 ppm after washing with NH_3. The ammonia wash stream from the separation section is set to 2.25 tonnes/hr to achieve this constraint.
- Maximum compressor speed of 10300 RPM and maximum outlet pressure of 155 barg. Lower operating constraints for the compressor are not considered as the reaction extinguishes before these become relevant.
- Min/Max flow of cooling water at ±25% of the nominal value for CW-1

2.3.2 Reaction section

In the reaction section the syngas is heated to the reactor operating conditions and converted to ammonia in the reactor. Surplus heat, not used for feed heating, is used for high pressure steam generation.

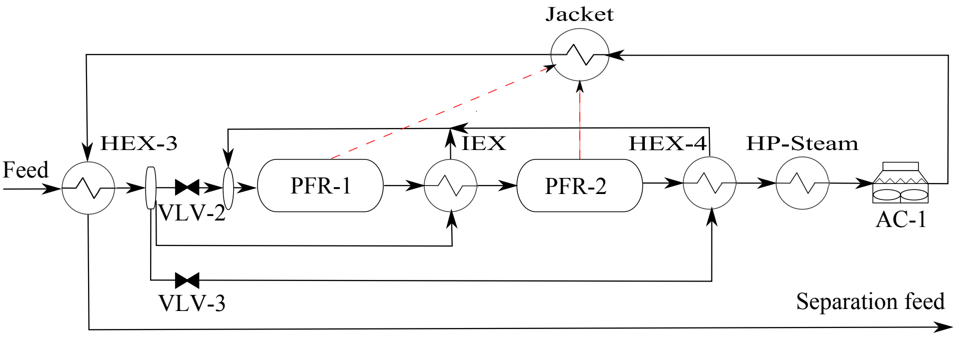

Figure 2.3: PFD for the syntehsis reaction section in the NH_3-plant.

Process description

The entering syngas feed from the makeup section is heated with the final product stream from the reaction (HEX-3) as shown in the PFD in Figure 2.3. The reaction section consists of a jacketed two bed tubular reactor with quenching between the beds (in heat exchanger IEX) and heat exchangers for heat integration and high pressure (HP) steam production.

After the heating of the feed stream with the product stream, it is split into three substreams, of which 2 are heated internally by the reactor effluent through heat exchangers IEX and HEX-4. The direct route for the syngas to PFR-1, through VLV-2, includes a fired heater to supply additional heating during plant start-up operations. During normal operation the process is autothermal, which means that all necessary heat in the reaction section is provided by the heat of reaction in the reactors and the heater is turned off. The split ratio of the sub streams is determined by valves VLV-2/3. The product stream from the reactor is further cooled after the quenching (HEX-4) by providing heating for the HP-Steam boiler and cooled by the air-cooler AC-1. This air cooler provides a fast reacting method of controlling the inlet temperature after HEX-3. The cooled product stream passes through the reactor jacket cooling the reactor beds before heating the reactor feed in HEX-3. Nominal reactor conditions are shown in Figure B.1 in Appendix B.2.

Cost contributors

The plant profits are generated in the reaction section with produced NH_3 and steam production. There are secondary costs related to the reactor operation such as catalyst regeneration and use of the fired heater. These are not considered for the cost of the plant operation. However with regards to the catalyst lifespan the reactor temperature is constrained to stay below 530°C.

Lower conversion in the reactor leads to a larger recyle syngas which increases the load on compressor C1-RE, which has an indirect effect on the cost. This also increases the flowrate through the reactors, reducing the residence time in the reactor and further lowering the conversion. A high temperature in the feed to the separation section increases the cooling need in this section, which also contributes to the cost.

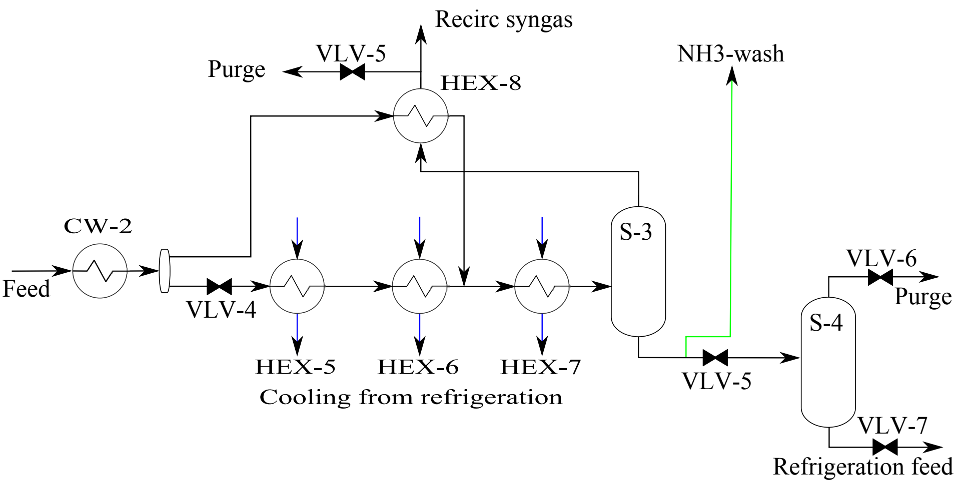

Figure 2.4: PFD for the NH_3 separation section.

Constraints

Constraints for the reaction section are:

- Reactor temperature limited to an upper temperature of 530°C. No lower temperature bound as the reaction extinguishes
- Flow of H_2O through the HP-Steam exchanger is limited to ±25% of the nominal operating value.

2.3.3 Separation section

After heat integration in the reaction section the reactor effluent is passed to the separation section where the ammonia is condensed out of the vapour stream at elevated pressure in heat exchangers using liquid ammonia from the refrigeration section as the cooling medium. The two phase stream is separated over separation tanks, the vapour phase is recycled as syngas with a part purged for inert gas control whilst the liquid, mainly ammonia, enters the refrigeration section.

Process description

Initially the feed stream from the reaction section is cooled with cooling water (CW-1) before the stream is split in two; this split ratio is controlled by valve VLV-4. The upper stream passes through HEX-8 and is cooled by the recycle syngas returning to the make-up section (reducing the cooling need from the refrigeration section). In the lower part cooling is provided from the refrigeration section over HEX-5/6 before the two product streams are combined and cooled with further refrigeration over HEX-7. The resulting two phase stream is separated in S-3, where the gas phase is returned to HEX-8 and heated before purging (to avoid accumulation of inert gases in the recycle) and returned to the syngas makeup section. Part of the ammonia liquid stream is returned to the syngas make-up section for water washing before it is returned to tank S-4. The remaining liquid stream enters S-4 directly. Valve VLV-5 and 7 are used for level control of S-3 and 4 respectively. VLV-6 controls the pressure in S-4.

There are considerable pressure drops over VLV-5 and VLV-7 that causes a temperature drop due to the Joule-Thompson [5] effect in the refrigeration feed stream and some of the dissolved inert gas components to evaporate, which are purged over S-4. This pressure let down and temperature change is used at the first stage of cooling in the refrigeration section.

Cost contributors

On the one hand a large degree of cooling in the refrigeration section increases the amount of produced liquid ammonia and decreases the amount of ammonia in the vapour recycle stream, which reduces the compressor work and improves the reactor conversion. However on the other hand, this raises the cost in the refrigeration section. Similarly with purging: a high purge ratio reduces the accumulation of inerts and hence the compressor power requirements, but simultaneously enhances the loss of valuable syngas. Thus there is a clear trade off that has to weighted, but maximum cooling seems beneficial to maximise the liquid ammonia production and as little as possible ammonia in the recycle syngas.

Constraints

Conctraints for the separation section are

- The wash stream of NH_3 is set in the syngas makeup section to guarantee adequate H_2O removal in the fresh syngas stream.
- The flow of cooling water in CW-2 is limited ±25% of its nominal value.

The flow of cooling ammonia to the heat exchangers in the separation section is determined in the refrigeration section. Therefore the cooling over HEX-5-7 is not included as a constrained manipulated variable for the separation section.

2.3.4 Refrigeration section

The liquid product stream from the separation section, mainly ammonia, is used as a cooling medium for the plant in the refrigeration section before it leaves the plant. In addition the last impurities of water and dissolved gases are removed in this section from the liquid ammonia product in addition to providing cooling. Cooling is provided by liquid ammonia at varying temperatures and pressures in heat exchangers. With four connections to the other plant parts and internal loops in the section the refrigeration represents the most intricate part of the plant.

The refrigeration section in the Yara plant is a semi-closed refrigeration system where the cooling medium ammonia circulates the section providing refrigeration before it passes on to storage. Other cooling configurations are open systems where the cooling medium is not cycled or closed loop systems, in which the produced ammonia is directly stored and the refrigeration loop is a thermodynamically closed system. The benefit of the semi-closed refrigeration system is the use of the cooling effect of the pressure let down of the product stream before it is stored and the final discharge of inert gases from the product stream.

Process description

The interconnectivity of the refrigeration section can be seen from the PFD in Figure 2.5 with several connections to the other plant parts and loops from the heat exchangers to the separation tanks. Nominal conditions and composition at various stages in this section are provided in Appendix B.4.

The incoming liquid/gas feed stream from the separation section is separated by separator S-5, where part of the liquid stream provides cooling for HEX-7 in the final cooling for the ammonia-separation and the remaining part of the liquid passes on to storage. The cooling cycle follows the same principle for S-6/HEX-6 and S-7/HEX-5/HEX-1. The vapour from the top of each tank is compressed in compressor C2 with the vapour from S-5 entering the compressor at the 1st stage, C2-1, the vapour from S-6 at the 2nd stage C2-2 and from S-7 at the third stage. The compression causes a significant temperature increase which is removed by interstage cooling in CW-3[3]. As for the reaction section compressors the refrigeration compressors are connected to the same axle, meaning that they run at the same speed. In the current configuration the compressor speed is manipulated to control the outlet pressure of the vapour phase in S-5. Appendix C.2 has a brief description of the refrigeration compressors. After the last stage of compression AC-2 and CW-4 cools the vapour stream which condenses the majority of the stream which is separated in S-8. The non-condensed ammonia in this vapour stream is furthermore cooled and separated through HEX-9 and S-9. The gas stream leaving S-9 mostly consist of inerts and this arrangement can be seen as further purification of ammonia.

Tanks S-6, S-7 and S-9 are elevated compared to the base level of the plant, and due the hydro (or "ammonia")-static column from the tank to the outlet valve there is a pressure increase. The liquids streams from the tanks to the heat exchangers passes over relief valves which reduces the pressure in the liquid stream, causing more evaporation of the ammonia in the exchangers. The same also applies for HEX-1; VLV-12 controls the outlet pressure from this heat exchanger.

Cost contributors

The main cost contributors in this section are the compressor operating costs and the cooling requirements over AC-2 and CW-4. These expenses are all necessary for the cooling utilities for NH_3-separation and the syngas-makeup.

Constraints

Limitations for the refrigeration operation are

- Max/min compressor speed of 6600 and 10300 rpm.
- Max/min suction pressure at compressor C2-1 inlet of 90 and 150 mbarg.
- Max/min cooling water flow for CW-3 and CW-4 at ±25% of the nominal value.

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[3] This cooling decreases the necessary compressor work to reach a given pressure compared to a warmer stream [26]

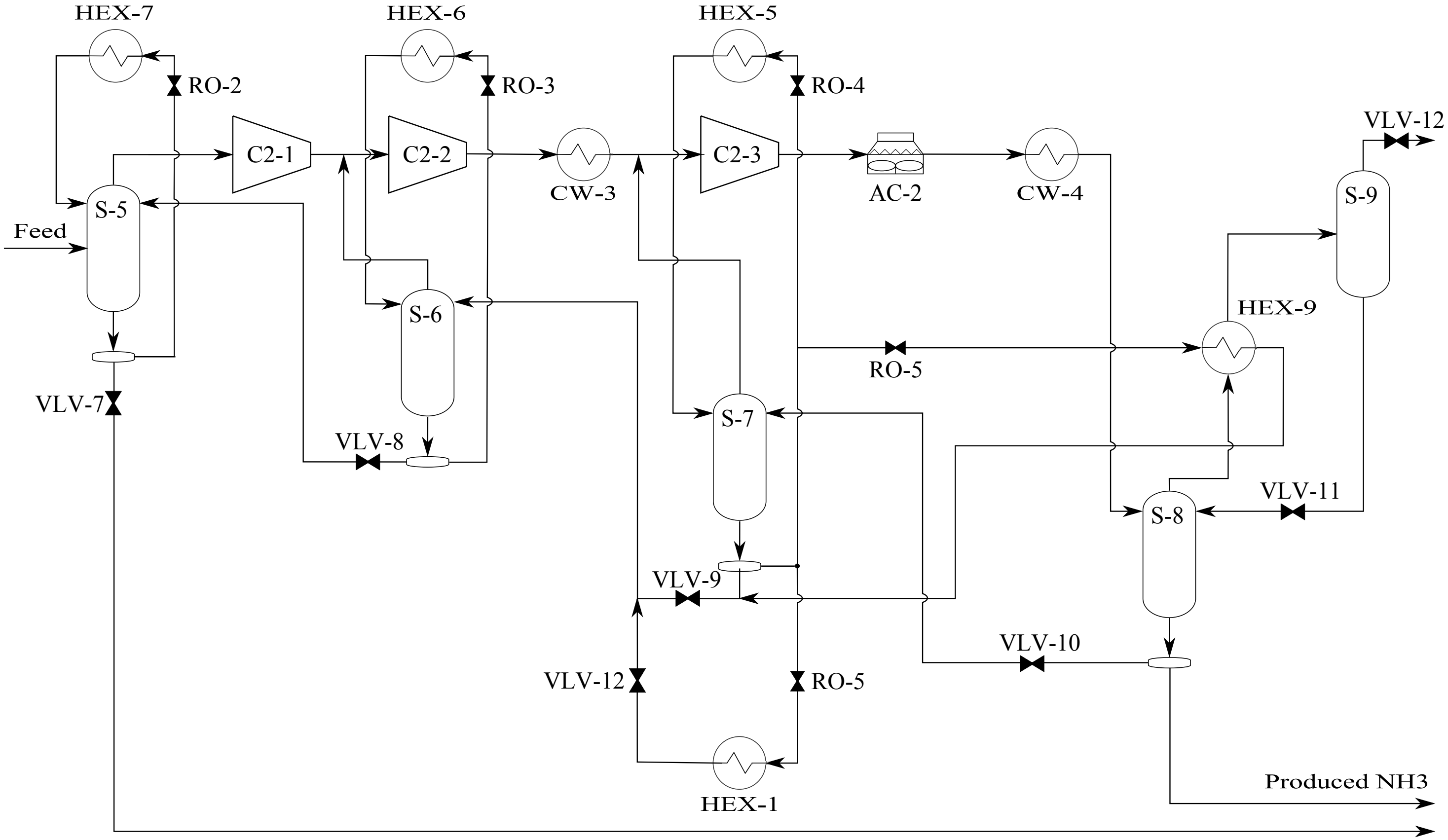

Figure 2.5: PFD for the NH_3-Refrigeration loop in the plant.

Chapter 3

Process Modelling

The process model was built in Hysys based on the process description in Section 2.3. Aspects and choices made for the modelling are described in this section. The set-up of Hysys for flowsheet optimisation using the MATLAB function `fmincon` are described in Section 4.5.

Modelling the Haber-Bosch NH_3 as a steady-state process proved more difficult and time consuming than anticipated at the beginning of the master project. Building a steady-state model that represented the nominal values reported by Yara was a relatively straight forward task, though some discrepancies were encountered in describing pressure let down over the relief orifices for the wash ammonia to the syngas make-up section. There were also some problems with the heat exchanger models. However the main issue was to develop a robust model that represented the whole range of process operating conditions of interest for the optimisation. These challenges are discussed as issues with the relevant units.

3.1 Thermodynamic model and kinetics

3.1.1 Fluid package

The basis for calculation of physical properties is defined by the selection of equations of state (EOS) for the system. These are predefined as fluid packages such as Soave-Redlich-Kwong (SRK) or Peng-Robinson (PR). Both fluid packages are defined from critical data for the components in the simulation environment (critical temperature and pressure) and can be modified by the user for specific needs, for example by modifying activity parameters. A non-ideal representation of the system is necessary to obtain a correct description of the activity (fugacity) and the compressibility in the unit operations, especially for the high temperature and pressure in the reaction section and the phase transitions in the separation section.

The SRK EOS handles systems with polar components like ammonia well, whilst PR is intended for applications in hydrocarbon processing. For the modelled ammonia system, SRK showed good correlation with reported data from Yara in the simulation and for reported data in literature [1] [21]. Simulations with another fluid package, PR, did not reproduce the same results with regards to liquid-vapor composition in the separation tanks. Thus, SRK was the choosen fluid package and no further modification was deemed necessary.

3.1.2 Reaction kinetics

Based on catalyst studies of the surface reaction for the ammonia synthesis reaction (2.1 on 6 the surface reaction can be formulated as the following dual-site (Langmuir-Hinshelwood) mechanism on the catalyst [14][20]:

$$\mathrm{N_2} + * \rightleftharpoons \mathrm{N_2} * \tag{3.1}$$

$$\mathrm{N_2} * + * \rightleftharpoons 2\mathrm{N} * \tag{3.2}$$

$$\mathrm{H_2}* \rightleftharpoons 2\mathrm{H} * \tag{3.3}$$

$$\mathrm{N} * + \mathrm{H}* \rightleftharpoons 2\mathrm{NH} * \mathrm{H} \tag{3.4}$$

$$\mathrm{NH} * + \mathrm{H}* \rightleftharpoons \mathrm{NH_2} \tag{3.5}$$

$$\mathrm{NH_2} * + \mathrm{H}* \rightleftharpoons \mathrm{NH_3} \tag{3.6}$$

where $*$ represents a vacant catalyst site on the surface. Studies indicate that the dissociative adsorption of N_2 on the catalyst surface, Equation 3.2, is rate determining (the slowest reaction step on the surface). If the adsorption of H_2 and the NH species on the surface are assumed to have no effect on the rate determining step; then the reaction rate for ammonia, r_{NH_3}, can be represented as [15]:

$$r_{\mathrm{NH_3}} = k_1 \phi_{N_2} - k_{-1} \frac{\phi_{NH_3}^2}{\phi_{H_2}^3} \tag{3.7}$$

ϕ_i is the fugacity of component i given by the SRK-EOS. The forward and backward reaction rate constants k_1 and k_{-1}, are calculated from the

Table 3.1: Activation energy and scaled reaction rate parameters for forward and backward reaction for Haber-Bosch NH_3-production from H_2 and N_2.

		r_1	r_{-1}
	E_a [J/mol]	$1.1 \cdot 10^4$	$1.1 \cdot 10^5$
PFR-1	A A'	1	$8.9 \cdot 10^{11}$
PFR-2	A A'	0.34	$3.1 \cdot 10^{11}$

expanded form of the Arrhenius equation:

$$k_1 = A \cdot \frac{\mathrm{e}^{\frac{-E_a}{RT}}}{T} \tag{3.8}$$

$$k_{-1} = A' \cdot \frac{\mathrm{e}^{\frac{-E'_a}{RT}}}{T} \tag{3.9}$$

where A and A' are the pre-exponential factors, E_a and E'_a are the activation energies for the forward and backward reaction respectively. The activation energies are the same for both the reactor beds in the simulation, but to account for different catalyst activities the pre-exponential factors differ between the beds, as shown in Table 3.1.

This power law representation is one of the simpler ways to model the kinetics for heterogeneous reactions on a catalytic surface and the simplified representation reduces the computational effort for the reactor bed calculations in the flowsheet simulations. For nominal conditions the rate expression shows good correlation with reported plant data, but it is important to keep in mind that expression will not be valid for a wide range of process conditions.

In HYSYS the chemical reactions and their kinetics are defined by selecting the reaction type and the stoichiometry of the reaction. Details for the EOS-description and reaction kinetics are given in the HYSYS thermodynamics guide [4].

3.2 Unit operations modelling

After selection of the fluid package and definition of reactions of interest the HYSYS model is defined by introducing the relevant unit operations, such as heat exchangers or separation tanks, based on the PFDs. The unit operations are connected with material or energy streams for the flows in the process. The units used in the simulation flowsheets are explained in the following section.

3.2.1 Compressors

All the compressors are reciprocating compressors based on the description in Appendix C. The characteristic curves necessary for defining the compressor operation where obtained from Yara. Due to the single drive shaft configuration for the syngas make-up and refrigeration compressors, the RPMs for each compressor in the compressor trains (C1 and C2) were fixed to the same value using a Hysys spreadsheet.

In all compressor applications surge lines, with a short closed loop around the compressor, are necessary for safe operation to avoid surging (flow disruption or reversal), which can cause damage to the equipment and surrounding personnel. These have not been included in the steady-state model as they do not offer any information in the steady-state, but are more of interest for dynamic behaviour or compressor operation studies.

Issues with the compressor model

For the steady-state model in Hysys the compressors have no effect on the upstream pressure or flow. There is only a downstream effect of the compressor operation and one implication of this is that it is possible to determine both the flow and outlet pressure from a compressor, which is unphysical. In reality increasing the compressor speed also gives greater suction and the flow through the unit. This means that the resultant pressure increase over the unit is less due to the decreased compressor head for larger volumetric flow (see the compressor curves and description in Appendix C). The effect of this is that the compressors in the Hysys model appear to be able give a large pressure increase for the system with a given feed rate.

Another pressure related weakness in the Hysys steady state model is that the pressure is set to the lowest value for stream combination over mixers in Hysys which caused the pressure to collapse throughout the reaction, separation and refrigeration section if the recycle pressure was lower than the discharge pressure from the high pressure compressor. .This made it necessary to fix the pressure of the recycle stream after heat integration in HEX-8 to the discharge pressure of the fresh feed from C1-HP with a negative pressure drop valve. Such that we get a "free" isenthalpic pressure increase (compared to the work required for compression) of the recycle syngas at lower compressor speeds. This occurs when the pressure of the recycle stream from S-3 drops below the outlet pressure of the high pressure compressor C1-HP. For the lowest compressor speed this pressure gain is 5 bar for the recycle gas stream.

In the dynamic model the discharge pressure from the compressor and outlet pressure from C-8 are equated in the simulation with pressure calculations. These are issues with a modular flowsheet solver such as HYSYS, where the structure of the flowsheet determines a sequential calculation order in which each process unit is solved. The solution is only dependent on the input flow conditions to the unit and there is no upstream effect from the solution of a process unit. This is in contrast to dynamic models and real systems where the flows are pressure driven and down stream units have an impact on the pressure profile and thus the flow characteristics through the system. With this in the consequence of these shortcomings in the modular approach is that the compressor operation window had to be limited to stay within the compressor curves.

These are intrinsic issues with the modular flowsheet approach, an equation oriented steady state model should be able to handle this effect as the entire flowsheet is solved simultaneously, these aspects are discussed in Section 3.4 as alternative modelling approaches.

3.2.2 Heat exchangers

All the heat exchangers including the cooling water (CW) and the internal exchanger in the reactor (IEX), are modelled as counter-current shell and tube heat exchangers. Their sizes and number of shell/tube passes are defined based on plant data. The heat transfer coefficient, UA, was selected to match the reported performance of the exchangers.

Issues with the heat-exchangers

It was deemed inadequate to use fixed pressure drops over the heat exchanging units as the performance largely hinges on the pressure profile of the system, especially for reaction and separation. It was initially attempted to model the pressure drop over the heat exchangers using friction factors (k-values) in the dynamic rating mode for a consistent way of defining the pressure drop over the units. Using this method however, the heat exchangers were prone to failing on initialisation or when moving away from the nominal conditions. This issue was resolved by changing the heat exchanger model to "Simple End Point" and the pressure drop over the unit was determined from the following empirical equation:

$$\Delta p_{new} = \left(\frac{\mu_{new}}{\mu_{ref}}\right)^{0.2}\left(\frac{\dot{m}_{new}}{\dot{m}_{ref}}\right)^{1.8}\left(\frac{\rho_{ref}}{\rho_{new}}\right)\Delta p_{ref} \tag{3.10}$$

Where μ is the viscosity, $\dot{m}$ the massflow and ρ the density. The reference values, ref, are the nominal values for the parameters and new the current conditions in the simulation. The reference and input (new) values were exported to a HYSYS-spreadsheet which calculated the new pressure drop, ΔP for the current state.

Also the heat exchangers were prone to failing for large differences in the tube/shell side streams over the exchangers, which causes a temperature approach in the heat exchangers that for some reason fails the heat exchange calculation. Especially the heat exchangers in the separation section were prone to crashing mostly mostly due to the fact, that the temperature can approach here for certain process conditions in the recycle iterations. Due to this the splits of the streams to the reactor over VLV-2/3 and in the separation section, VLV-4, were only optimised for a small range of values around the nominal split as large deviations from the nominal split values caused the heat exchanger calculation to fail.

3.2.3 Separation tanks

The separation tanks were all modelled as HYSYS separators based on Yara sizing data and perfect separation of the liquid and vapour phases is assumed. The syngas make-up tanks S-1 and S-2 are vertical tanks due to the large proportion of gas in the tank streams, conversely the separation and refrigeration separation tanks are horizontal (S-3 to S-9). The phase calculations are carried out at the pressure of the lowest incoming product stream with no pressure drop over the tank. There were no issues with modelling the separation tanks.

3.2.4 Valves and relief orifices

The VLV valves are modeled as linear manipulated valves. These valves are assumed to be isenthalpic and the pressure drop over the valves are calculated from the valve characteristics (k-values) determined to match plant data.

Also the pressure relief orifices in the simulation flowsheets were modelled as linear manipulated valves with a fixed opening position and valve k-values to match the orifice pressure drop at nominal conditions. This was done as the orifices (relief valves with fixed cross sectional area) would not calculate pressure drops for flows of magnitude outside the nominal conditions.

Issues with the valves

In the actual or dynamically modelled plant operation the split of streams is determined by the pressure gradients. The split ratio is then manipulated by changing valve positions on the split streams. For the steady-state modelling these have to be specified by the split TEE's and the valves only add the stream pressure drop. Thus changing the split ratio at a TEE does not represent a change in the pressure dynamics on flow manipulation as the valve position does not change with the TEE split.

3.2.5 Reactor

The two reactor beds are modelled as two PFR reactors with the kinetics introduced in Section 3.1.2. The pressure drop over the reactor is determined by the configuration for passing the syngas over the catalyst and catalyst properties such as configuration in the reactor, surface properties and particle shape. Similarly the heat transfer from the reacting beds is determined by the configuration and properties of the reactor cooling. However due to limited data on the reactor internals the modelling of the pressure drop and cooling trough the jacket was limited to constant values chosen to match the plant data at nominal operating conditions. These values were a cooling duty of 500 kW and pressure drop of 0.4 bar over each bed.

3.2.6 Air coolers

AC-1, the reaction air cooler, is modelled as a two fan unit whilst AC-2 is a four fan unit with air flow capacity and heat transfer coefficients given from Yara. The fan speed for the each of the individual fans in the coolers are fixed to the same value using a HYSYS spreadsheet, this was done for easy adjustment of the fan cooling in the optimisation routine. The inlet air temperature and pressure was set to 25°C and 1 bar.

3.2.7 Pumps

In the steady-state HYSYS model the elevation of process units does not have any impact on the pressure increase for the flow to a downstream unit due to hydrostatic pressure from the fluid column. This flaw was compensated for by introducing pumps to the flowsheet model for the elevated

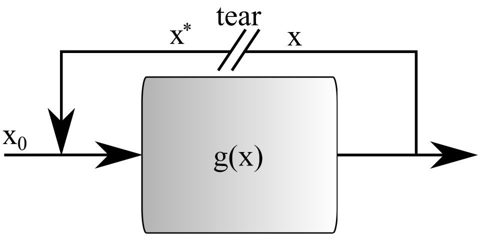

Figure 3.1: The input/output structure for a tear stream/recycle block. x* is the guessed state of the stream whilst x is the calculated state. g(x) may represent several unit operations.

tanks S-5, S-6, S-7, and S-9 which are all in the refrigeration section. The pressure increase was kept constant at the nominal value as the composition and temperature and thus the density of the liquid outlet streams remained close to the original value for the optimisation.

A more detailed description of the basis for modelling units in HYSYS is available in the HYSYS operations guide [3].

3.3 Recycle loops

A key feature with modular flowsheet descriptions is the need for tear streams to solve for downstream flow dependencies for a upstream process unit, such as a recycle stream or heat integration. This dependency is "broken" by introducing a tear stream or recycle block which iterates the torn stream to convergence for a certain tolerance for the process variables. The process is conceptualised in Figure 3.1 and the tear stream solves for x* so that:

$$x = g(x_0, x^*) \quad \text{or} \quad f(x, x_0, x^*) = x - g(x^*, x_0) = 0 \tag{3.11}$$

The implicit function is typically solved using a Newton-Raphson or Broyden method for iteration to a solution within tolerances [9][22].

In HYSYS the recycle block is implemented as a theoretical unit operation which guesses a value for the torn stream, x^*, calculates a new value with the guessed stream $g(x^*, x_0)$ and compares these. Based on the difference a new value is calculated $g(x^*, x_0)$). This method is iterated on until the difference of the two streams is within tolerances set by the user or a maximum number of iterations is reached. In the ammonia plant model the recycle block

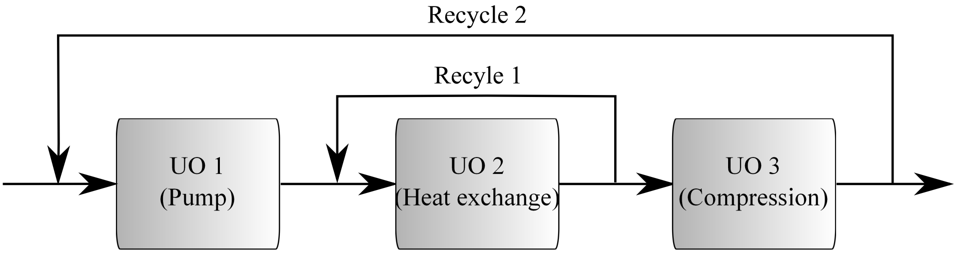

Figure 3.2: Illustration of a nested recycle loop with example units operations.

positions were selected with two aims in mind, a minimal number of recycle blocks subject to no twice broken streams. This was done to minimise the time required to converge the flowsheet to a new steady state, as it reduces the number of times each nested recycle block has to be evaluated [9].

One of the main challenges and issues with the optimisation of the ammonia plant model were the nested loops in the problem and Figure 3.2 shows the concept of a nested loop in the flowsheet. The nested structure gives that the inner loop has to be solved for each iteration in the outer loop, which can make the required number of iterations to solve the flow sheet huge. Also the accuracy of the solution is impaired with the recycle tolerances in each recycle block in the loops. An example of a nested loop in the ammonia plant is the reaction section heat integration, in Figure 2.3 on page 13, where there is an internal loop for heat over the internal heat exchanger (IEX) that sits inside the heating of the feed with HEX-3.

The challenge with regards to model stability was that the iterative technique used for the optimisation often guessed a tear variable that was an order of magnitude smaller or larger compared to the original stream. This caused the flow sensitive unit operations to calculate unphysical values such as the valves giving negative pressure due to too high pressure drops. Also there was problems with the heat exchangers as large flow differences in the cooled and heated stream caused a temperature approach of the outlet stream which failed the heat exchanger. This halted the flowsheet simulation and broke the optimisation routine. The solution around this was to chose an optimisation method (interior-point) that made small perturbations in the manipulated process variables and to set the pressure drop over the valves to fixed values. Further challenges with the recycle with regards to optimisation are discussed in Section 4.5.

3.4 Alternative modelling approach

An alternative steady state modelling approach that avoids the introduction of tear streams and iterations in nested loops is an equation oriented model where the full set of plant equations (mass and energy balances, equipment specifications, reaction and thermodynamic model etc) are cast into a sparse matrix system. The benefit of equation oriented modelling is that the entire system is solved simultaneously and gradients for the optimisation problem are readily available. However developing the model is much more demanding compared to the modular mode and the initialisation of the equation oriented approach can be difficult especially with the large scale and number of variables for the ammonia plant [9].

Chapter 4

Optimisation

This chapter presents the economical optimisation problem and method of optimisation based on the process model described in the previous section. Optimisation in plant operation is key to identifying the best (optimal) operating point. This is the basis for defining the control objective and starting point for designing the control structure to achieve this target. One example is self-optimising control where the aim is to achieve acceptable deviation from optimal operating point for disturbances with a constant set point policy as described in chapter 10 of [28].

An alternative goal for optimisation, besides maximising profits, may be to minimise the environmental impact by reducing emissions related to plant operation with operating costs and production as constraints. Ammonia production has a significant environmental impact with emissions of CO_2 and other harmful components such as SO_x and NO_x from syngas preparation [6]. For many aspects economical and environmental optimisation go hand in hand for the goal producing more product with less consumption of utilities and feedstock and this study focuses on economical optimisation.

4.1 Problem definition

The objective for the economical optimisation is to minimise a cost function, J, typically given as:

$$\mathrm{J} = C_{\mathrm{Feed}} + C_{\mathrm{Utilities}} - C_{\mathrm{Income}} \quad [€/\mathrm{hr}] \tag{4.1}$$

where C_i is the cost or profit of a cost contributor as identified in the Plant Description in Section 2.3.

The optimisation problem is then defined by formulating the minimisation of J whilst satisfying a set of constraints given for the problem. This non linear problem can be written as:

$$\begin{aligned} \min_{\mathbf{u}} \quad & \mathrm{J}(\mathbf{x},\mathbf{u},\mathbf{d}) \\ \text{s.t} \quad \mathrm{c}_i(\mathbf{x},\mathbf{u},\mathbf{d}) &= 0 \quad i \in \mathcal{E} \\ \mathrm{c}_i(\mathbf{x},\mathbf{u},\mathbf{d}) &\leq 0 \quad i \in \iota \end{aligned} \tag{4.2}$$

Where c is the set of constraints to be satisfied, with indices $\mathcal{E}$ denoting the equality constraints and ι the inequality constraints. $\mathbf{x}$ represent the internal state variables (e.g temperature pressure or molar flows) determined by HYSYS, $\mathbf{u}$ is the set of decision variables or degrees of freedom that the optimiser adjusts to obtain the optimal solution, and $\mathbf{d}$ is the set of disturbances. The nature of the disturbances means that they are not determined at any instance, but for the purpose of optimisation these can be inputs to the optimisation problem to determine the sensitivity of the optimal solution to the disturbances, for example changing the molar ratio of H_2/N_2 in the feed or the feedrate, as a case study.

The state variables $\mathbf{x}$ are solved separately in the model and separated from the optimisation problem. An example of this is the solution of recycle tear streams that are solved in the flowsheet simulation. However it has been shown that letting the optimiser solve for these may be beneficial and even necessary to guarantee a successful optimisation [7] [10]. This can for example be achieved by setting the recycle tear stream as an equality constraint, such as $x^* - g(x, y) = 0$ in the recycle example in Figure 3.1. It should be noted that the alternative approach of letting the optimiser find the solution to the recycle tear streams, by defining these as equality constraints, does not guarantee for a solution to the optimisation problem without properly selected tear streams. With the number of components and loops in the ammonia plant the definition of all these as equality constraints is not trivial. It does however offer better control of the convergence criteria of the recycle convergence criteria, as it is controlled as the equality constraint tolerance criteria (`'TolCon'` option in `fmincon`)

For the optimisation in this study $\mathbf{x}$ was kept separate from the optimisation routine and the cost-function, J, and the constraints, $\mathbf{c}$, are only dependent on the input, solved for the optimiser, and disturbances $(\mathrm{J}(\mathbf{u},\mathbf{d})$

and c($\mathbf{u}, \mathbf{d}$)).

4.2 The optimiser

The MATLAB function `fmincon` was used for finding the optimal solution to the problem formulation in Equation 4.3 for the HYSYS flowsheets and the following section describes aspects with the optimisation routine.

The interior point (IP) method was selected as the optimisation method as this was the recommended initial algorithm for `fmincon` [24][25]. This method guarantees that each step in the process model is a feasible step that satisfies the constraints for the problem with the introduction of a barrier function. The barrier function causes the objective function to approach infinity as the constraints approaches their bounds. The optimal solution is then found using a Newton-Raphson type iteration on the reformulated problem to obtain a solution that satisfies the optimality conditions in Equation 4.4. The sequential-quadratic-algorithm (SQP) was also tested but this algorithm had a tendency to make large perturbations in the HYSYS decision variables which took a long time to converge in the simulation environment and the simulation failed, if the steps where too large. Both IP and SQP methods are described in chapter 6 of [7].

IP and SQP utilise Lagrangian multipliers which are introduced in the optimisation routine to find the optimal solution that satisfies the constraints of the problem. The modified optimisation problem, L with the Lagrange multipliers $\boldsymbol{\lambda}$, can be written as:

$$\boldsymbol{L} = \mathrm{J}(\mathbf{u}, \mathbf{x}, \mathbf{d}) - \boldsymbol{\lambda}^{\boldsymbol{T}}\mathbf{c}(\mathbf{x}, \mathbf{u}, \mathbf{d}) \tag{4.3}$$

The optimal solution is then characterised by the Karush-Kuhn-Tucker (KKT) conditions which are defined as [7]:

$$\begin{aligned}
\boldsymbol{\nabla}_{\boldsymbol{x}}\boldsymbol{L}(\mathbf{x}^*, \mathbf{u}^*, \boldsymbol{\lambda}^*) &= \mathbf{0} \\
\mathrm{c}_{\boldsymbol{i}}(\mathbf{x}^*, \mathbf{u}^*) &= \mathbf{0} \ \text{ for all } \ \boldsymbol{i} \in \boldsymbol{\epsilon} \\
\mathrm{c}_{\boldsymbol{i}}(\mathbf{x}^*, \mathbf{u}^*) &\geq \mathbf{0} \ \text{ for all } \ \boldsymbol{i} \in \boldsymbol{\iota} \\
\boldsymbol{\lambda}_{\boldsymbol{i}}^* &\geq \mathbf{0} \ \text{ for all } \ \boldsymbol{i} \in \boldsymbol{\iota} \\
\boldsymbol{\lambda}_{\boldsymbol{i}}^*\mathrm{c}_{\boldsymbol{i}}(\boldsymbol{x}^*, \boldsymbol{u}^*) &= \mathbf{0} \ \text{ for all } \ \boldsymbol{i} \in \boldsymbol{\epsilon} \cup \boldsymbol{\iota}
\end{aligned} \tag{4.4}$$

where $\mathbf{x}^*$, $\mathbf{u}^*$ and $, \boldsymbol{\lambda}^*$ are the variables at the optimal solution. The KKT-conditions give an effective way of assessing the validity of the optimal solution from the solver.

Analytic gradients are inaccessible with the problem formulation in HYSYS. `fmincon` therefore estimates these by finite difference approximations and the convergence criteria are met when the estimated gradients and Lagrangian satisfies the tolerance criteria of the `fmincon` routine. It was also necessary to scale the decision variables due to the magnitude difference between the variables, e.g there is a order of three difference between the initial cooling flowrates and split ratio. This was done to reduce the sensitivity in gradient estimation for `fmincon` for certain (large norm) variables in the optimisation. On completion of an optimisation the run-time and total number of plant and optimiser iterations were registered to compare the performance of the different optimisation strategies. The code for the implementation of `fmincon` and settings for the IP-method are available in Appendix D.1.

4.3 Optimisation strategy

The optimisation routine is applied to a reduced model of the full plant. The idea of the subdivision is to study the performance of optimisation of subunits compared to an optimisation of the entire plant. One example of a subdivision may be to focus on optimising the operation of the reactor and syngas makeup section. The subdivision results in a less demanding optimisation as the model computational demand is less and there are fewer nested loops and decision variables for the optimiser to consider. However one might end up with conflicting results in the optimisation of interconnected plants if the objective is simply set to minimise the cost for a single subunit. For example an optimisation of the separation section may demand as much cooling as possible to increase the condensation of ammonia to the liquid product stream, whilst an optimisation of the refrigeration section may find that as little cooling might be deemed beneficiary as this would represent the least cost for this section if it is analysed in an isolated manner. The aim (the formulation of the cost function) and constraints for the optimisation therefore has to be rigorously examined and selected to avoid conflicting objectives in the subdivided optimisations. Also plant separation adds input or outputs to the system where interconnected streams are broken, these would have to be regarded as disturbances in the new system.

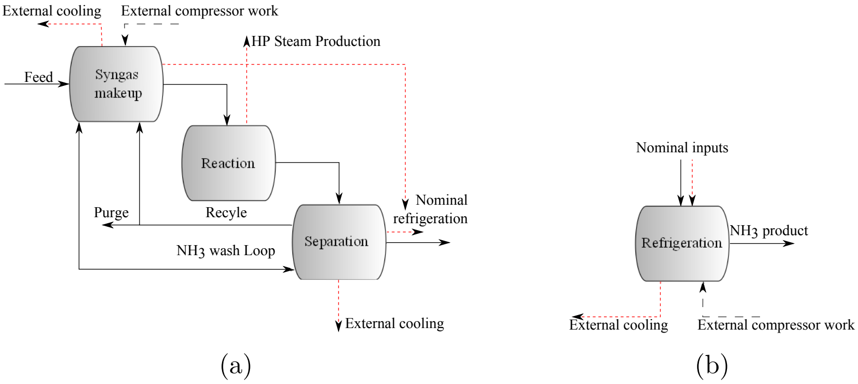

Figure 4.1: Subset 1 division of the ammonia plant for optimisation.

In recycle systems where there is originally a loop, it may be possible to replace the broken loop with a simplified model of the detached units. Surrogate and reduced models are widely used for efficient incorporation of detailed process models, for instance a computational fluid dynamics (CFD) model of a reactor, in an optimisation routine [8] [12]. These strategies have been developed for full replacement of more advanced (computationally demanding) models and not separation of the studied system. However, it is of interest to research whether simplified models can be used to find optimal conditions for integrated plants.

The following subsections describe the selection of subdivisions for the optimisation strategies.

4.3.1 Subset 1

The first subset division separates the refrigeration section as an independent optimisation task, as shown in Figure 4.1. Figure 4.1(a) attempts to optimise the makeup, reaction and separation section with the delivered refrigeration kept at the nominal values. Then the refrigeration section (Figure 4.1(b)) is optimised individually with the feed stream and cooling at nominal conditions.

Treating the refrigeration section separately greatly reduces the total number of nested loops in the simulation. This should result in a computationally less demanding optimisation.

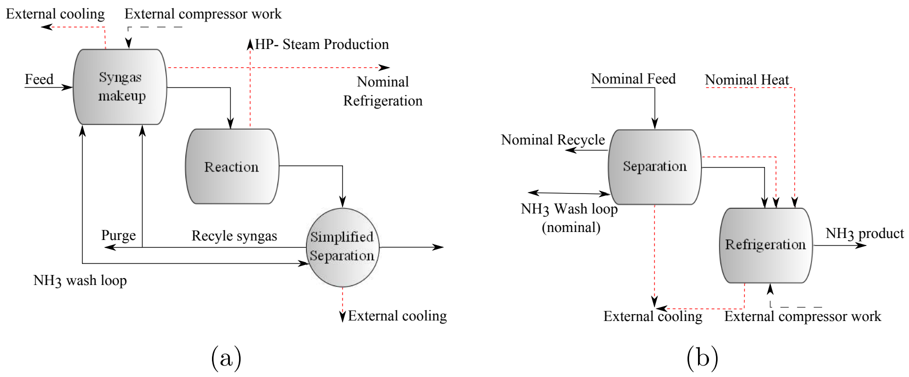

Figure 4.2: Subset 2 division of the ammonia plant for optimisation.

4.3.2 Subset 2

A weakness with the approach to optimisation in Subset 1 is that the separation results in a poor representation of the heat exchange between the separation and refrigeration section heat exchangers (HEX-5-HEX-7). To remedy this, a 2nd subset was selected as shown in Figure 4.2, in which the makeup and reaction section are optimised separately with a simplified model of the separation section (to include the effect of the purge ratio and recycle conditions in the optimisation for these sections), this separation is illustrated in 4.2(a).

The simplified refrigeration section replaces the series of heat exchangers with two heat exchangers, one for the cooling of the reactor product stream prior to separation in S-3 and the 2nd for the heating of the recycle stream (S-4 is omitted from the simple model). The cooling is provided with cooling water and heating with the nominal stream through HEX-8.

The 2nd subset in Figure 4.2(b) handles all the phase separations and six of the nested recycle loops in the flowsheet. The input to the subset is the reaction section product (prior to CW-2).

4.4 Optimisation problem

The optimisation requires the definition of the cost function, decision variables and process constraints as input to the optimiser routine for each subset. The first subsets (a) in Figure 4.1(a) and 4.2(a) are optimised for

Table 4.1: Relative costs of plant utilities per tonne compared to the value of ammonia per tonne.

Cost	Scaled cost $\boldsymbol{C_i/C_{\mathrm{NH_3}} \cdot 100}$
NH_3	100
Syngas	60
CW	0.8
HP-Steam	4
MP-Steam	3.2

the following cost function:

$$\mathrm{J}_{(\boldsymbol{a})} = \boldsymbol{C}_{\mathrm{HP}}\dot{\boldsymbol{m}}_{\mathrm{HP-}} + \boldsymbol{C}_{\mathrm{CW}}\dot{\boldsymbol{m}}_{\mathrm{CW}} - \boldsymbol{C}_{\mathrm{NH_3}}\dot{\boldsymbol{m}}_{\mathrm{NH_3}} - (\boldsymbol{C}_{\mathrm{HP}} - \boldsymbol{C}_{\mathrm{MP}})\dot{\boldsymbol{m}}_{\mathrm{HP+}} \tag{4.5}$$

and subsets (b) in Figure 4.1(b) and 4.2(b) for:

$$\mathrm{J}_{(\boldsymbol{b})} = \boldsymbol{C}_{\mathrm{HP}}\dot{\boldsymbol{m}}_{\mathrm{HP-}} + \boldsymbol{C}_{\mathrm{CW}}\dot{\boldsymbol{m}}_{\mathrm{CW}} - \boldsymbol{C}_{\mathrm{NH_3}}\dot{\boldsymbol{m}}_{\mathrm{NH_3}} \tag{4.6}$$

where $\dot{\boldsymbol{m}}_{\mathrm{HP-}}$ is the total steam consumption from the turbine powering C1 for $\mathrm{J}_{\boldsymbol{1(a)}}$ and C2 for $\mathrm{J}_{\boldsymbol{1(b)}}$ (as described in Appendix C.3). $\dot{\boldsymbol{m}}_{\mathrm{HP+}}$ is the steam produced after the reactor in unit HP-Steam from medium pressure steam (therefore the MP-steam price is subtracted from HP price in the cost function). $\dot{\boldsymbol{m}}_{\mathrm{CW}}$ is the total mass flow of cooling water in each subset, $\dot{\boldsymbol{m}}_{\mathrm{NH_3}}$ is the mass flow of ammonia in the product stream leaving each subset. $\boldsymbol{C_i}$ is the scaled cost related to each unit, these are presented in Table 4.1. Syngas is not included in any of the cost functions as it has been kept constant for the cases studied. If we regard the input feedrate as a disturbance the production will be maximised as the ammonia production is included in all of the cost function formulations.

The identified degrees of freedom or manipulated variables that are not used for inventory control are the decision variables. These are the variables that are adjusted to optimise the cost function and these are presented in Table 4.2 with the bounds for the optimisation.

Two of the manipulatable streams where fixed; the wash stream of ammonia was set to a flow of 2.25 tonnes to ensure proper water and carbon dioxide removal for catalyst longevity and the direct pass to the reactor was fixed as the through flow is very small in the nominal case and the maximum heat recovery is obtained with heat integration of the reactor effluent. The optimisation is bound by the constraints in Table 4.3.

Table 4.2: Decision variables for optimisation.

Decision variables	Initial	Max	Min
CW-1 Cooling w. [tonne/hr]	601	752	450
C1-HP Discharge [rpm]	102280	9950	12000
Split VLV-2/VLV-3	0.601	0.550	0.650
HP-Steam production [tonne/hr]	138	104	173
AC-1 Demand Speed [rpm]	173	100	300
CW-2 Cooling w. [tonne/hr]	725.9	544.4	907.4
Split ratio VLV-4 (HEX-8/HEX-5)	0.54	0.60	0.45
Purge ratio VLV-5 [-]	0.0172	0.015	0.018
C2 Compressor speed [rpm]	7736	10180	7000
CW-3 Cooling w. [tonne/hr]	399.2	500	300
CW-4 Cooling w. [tonne/hr]	1500	1875	1125
AC-2 Demand speed [rpm]	173	300	100

Table 4.3: Constraints for optimisation.

Description	Value
S-5 Outlet vapour	Max 5 ppm H_2O
Max discharge pressure C1-RE	155 barg
Max reactor T	530 °C
Split VLV-2/VLV-3	Total split ratio must sum to one and no negative split values
Split VLV-4	Total split ratio must sum to one and no negative split values
Max pressure S-3	152 barg
Max Steam consumption C2	50 tonne/h
Min suction pressure C2-1	90 mbarg
Max suction pressure C2-1	150 mbarg

The distribution of decision variables in Table 4.2 and constraints in Table 4.3 to the optimisation subsets is as follows:

Subset 1(a) Contains the decision variables from CW-1 cooling water flow to the purge ratio VLV-4 and is constrained by the S-5 outlet content of water to the maximum outlet pressure of S-3.

Subset 1(b) Is optimised with the decision variables from C2 compressor speed to the AC-2 air cooling fan speed. This set is constrained by the maximum steam consumption in C2 and maximum and minimum suction pressure for compressor C2.

Subset 2(a) Has the same decision variables and constraints as Subset 1(a) but instead of the CW-2 cooling rate and stream split in the separation section, the cooling in the simplified separation model is included as a decision variable.

Subset 2(b) Consists of the same decision variables and constraints as Subset 2(b) with CW-2 and the split ratio over VLV-4 as decision variables.

4.5 Setting up Hysys for optimisation

The identified cost function, decision variables and constraints for each of the process subset are exported to spreadsheets in their respective HYSYS models. These spreadsheets define the input/output structure between HYSYS and the MATLAB `fmincon` optimisation routine. The interface for relaying of outputs from the model and inputs from the optimiser, provides an easily accessible method for integrating the HYSYS process model and `fmincon` optimiser, as they are all gathered in the same spreadsheet format. It also alleviates the job of passing the decision variables to the different units easier as they are all available in the same column. The different spreadsheets and the role of these in the optimisation are given as follows:

Cost Function contains the defined cost function for the subset model and calculates a cost based on the plant simulation result which is exported from HYSYS as the objective function for `fmincon`.

Input handles the input of decision variables from `fmincon` to the HYSYS model. This spreadsheet also contains the starting (nominal) point for the optimisation and the lower and upper bounds for the decision variables that are imported by `fmincon`. The input scaling is handled with a scaling and a descaling function for input passing between HYSYS and `fmincon`.

Constraints evaluates the constraint functions to determine if they are satisfied for the current decision variable input.

The connection between HYSYS and MATLAB is handled by the Component Object Model (COM) in ActiveX that creates a HYSYS interface connection in MATLAB to the open HYSYS flowsheet[1]. Examples for the structure of the spreadsheets are given in E with MATLAB code for `fmincon` and supporting functions in Appendix D.1

Hysys optimisation challenges

Optimising the HYSYS spreadsheet with MATLAB offers challenges that need to be addressed for a successful optimisation and these are presented here.

One of the main issues is related to the large number of nested loops in the process model. The many recycle blocks are slowly converging and require many iterations to find the solution to the tear stream problem, even to the point where the HYSYS solver passes the maximum number of iterations and halts the simulation. This is alleviated by increasing the number of maximum number of iterations per recycle block. Also the error tolerances in the recycle blocks add inaccuracy to the numerical estimates of the gradient functions in the optimiser and the nested nature of the recycle loops augments this effect [11]. Further tightening constraints on the convergence criteria for the recycle blocks reduces this impact, but then increases the required amount of iterations to converge the recycle stream. Additionally this numerical inaccuracy causes numerical noise which may cause the optimiser to terminate prematurely at a non-optimal solution [7].

The weakness of inaccurate gradient estimations with the finite difference approach, could be resolved with access to the underlying model equations for the various unit operations but these are not available in commercial modular simulators as they are regarded as trade secrets. To verify that the operating point identified by `fmincon` was a true minimum, the solver routine was restarted with the proposed optimal point as the initial guess

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[1] More details about integrating HYSYS with 3rd party programs is available in the HYSYS customisation guide [2].

in the optimiser and also with different initial conditions further away from the optimium compared to the initial point.

The flowsheet topology defined in the simulation defines a strict calculation order which hinders flexibility for the optimisation routine calculations [10]. This is attempted to be alleviated with the plant separation strategy, but in each subset the calculation order is still defined though for a smaller set of units.

Another major issue is the lacking ability to automatically recover the simulation from infeasible process conditions in the optimisation routine without manual (user) intervention. This means that every iteration in the optimisation sequence has to be feasible and evaluated in the process simulation environment, which can cause considerable inefficiency for the optimisation routine [10]. Even with interior-point method and the constraint formulation in `fmincon` these have to be passed to the HYSYS simulator to evaluate if the constraints are satisfied. Thus the constraints are only applicable for "soft-constraints", that are feasible in the process simulator, but not acceptable as process conditions (e.g a reactor temperature over 530°C). This means that any combination (at least in the direction of the optimal solution) of decision variable inputs have to be feasible in the simulation and the bounds for these variables have be carefully evaluated.

Chapter 5

Results of optimisation

The results of the optimisation and the significance of these results are discussed in the following sections

5.1 Subsets 1(a) and 2(a)

Optimisation of the syngas makeup, reaction section and refrigeration section for subset 1(a) and the simplified model in subset 2(a) yielded the results in Table 5.1 and 5.2 on the next page. Both optimisations were successful in increasing the income by 10% for Subset 1(a) and 5% for 2(a) for the scaled cost variables. The optimisations achieved this by minimising the use of the external cooling utilities, maximising the steam production and finding the optimal point of operation for the compressor and split ratios. For 2(a) the cooling in the simplified representation of the separation did not approach the lower bound as the increased amount of ammonia in the vapour recycle stream reduces both conversion to ammonia in the reactor and recovery of ammonia in the reactor and separation stream. The variation in income is mainly due to the costing difference for the cooling section refrigeration.

Table 5.1: Optimisation results for Section 1(a).

Decision variable	Nominal value	Optimal	Comment
CW-1 cooling [tonne/h]	601.2	451.3	Lower Bound
C1-HP [rpm]	10283	10012	
Split VLV-2/3 IEX [-]	0.600	0.579	
HP-Steam prod. [tonne/h]	138	173	Upper Bound
AC-1 Speed [RPM]	173	215	
CW-2 cooling [tonne/h]	725.9	544.6	Lower Bound
Split HEX-8/9 [-]	0.535	0.520	
Purge Ratio [-]	0.0172	0.0163	
Cost	-3246.4	-3582.3	
$\mathbf{NH_3}$ [tonne/hr]	50.63	50.7	
Optimiser performance			
Function evaluations	-	851	
Run time [min]	-	18.1	

Table 5.2: Optimisation results for Section 2(a).

Decision Variable	Nominal value	Optimal	Comment
CW-1 Flow Rate [tonne/h]	601.2	451.3	Lower Bound
C1-HP [rpm] [tonne/h]	10283	10294	
Split VLV-2/3 IEX [-]	0.601	0.586	
HP-Steam Prod [tonne/h]	138	173	Upper Bound
AC-1 Speed [rpm]	173	231.4	
CW-Simple sep. [tonne/h]	832.3	748.9	
Purge ratio [-]	0.0172	0.0164	
Cost	-3663.7	-3842.9	
$\mathbf{NH_3}$ [tonne/hr]	50.70	50.94	
Optimiser performance			
Function evaluations	-	452	
Run time [min]	-	7	

Table 5.3: Reactor feed (PFR-1) conditions for Subset 1(a) and 2(a) in the optimal point compared to nominal conditions.

	T[°C]	p [barg]	$\dot{n}$[kmol/h]	$\frac{H_2}{N_2}$
1(a)	352.8	117.6	31015	3.15
2(a)	376.3	138.4	29378	3.16
Nominal	374.1	137.4	30052	3.15

The main difference between the two optimisations with regards to process conditions is the compressor operating duty which is reduced for 1(a) and increased in 2(a) from the initial point which causes a significant temperature and pressure difference in the feed to the reaction section, as shown in Table 5.3. However the ammonia production is only effected to a small degree for the different reaction conditions, this is shown with the production of ammonia in both reactor beds for the optimisations in Figure 5.1. This indicates that the reaction kinetics are insensitive to the conditions for the range of decision variables. For both optimisation results the conversion of ammonia almost reaches equilibrium independently of the inlet conditions. This is is similar to the nominal reactor profile in Figure B.1 on page 64. This shows that the rate expression in the Hysys model is insensitive to changing process conditions, especially temperature and pressure, compared to what one would expect from literature [1]. This results in an almost constant production rate of ammonia from the reactor, of 50 tonne/hr, with a fixed feed rate and very similar split factors in the two optimisations for the reactor feed split over VLV-2/3 and purge ratio.

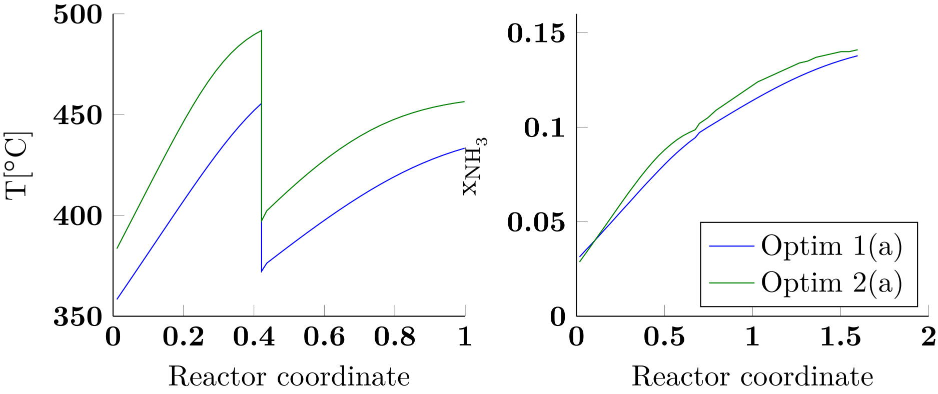

Figure 5.1: Reactor profile for optimisation 1(a) and 2(a).

The last remaining unbounded decision variable is the fan demand speed for AC-1, which has little impact on the process in the steady state. Changing the demand speed between the lower and upper bound, with the other decision variables kept constant in the optimal point, only changes the temperature drop of 40°C on the HP-steam outlet stream by 1°C and hence has negligible impact on the cost function. This cooling however plays an important role in temperature control of the reactor feed stream in the dynamic model and real plant. Further testing of the fan unit outside the lower and upper fan speed bounds showed that the temperature remained almost constant at 40°C except for a speed approaching zero.

The result of minimising or reducing the cooling utilities is slightly counter-intuitive. From a process engineering point of view, one would think that maximising the cooling prior to the compressor (CW-1 cooling) reduces the compressor operating costs with a lower inlet temperature. Also maximising cooling prior to separation (CW-2 cooling) would increase separation which increases production of ammonia and selectivity as there is less ammonia in the recycle. This seems to be caused by the relatively expensive cooling (which is typically regarded as a cheap utility) compared to the compressor operating cost and the income for produced ammonia.

There are two possible reasons for this:

- The cost of cooling water seems too high. Typical cooling water costs are reported as a factor 10 smaller than those reported for the plant, admittedly with large dependencies on geographic region and makeup costs [29].
- The magnitude of the cooling streams are very large causing high costs. These were set to match the reported heating duty of the heat exchangers for the given heat transfer number and may have caused excessive cooling flows, for example the nominal flow of cooling water through CW-1 is 3 times the design value. Thus there might be a significant mismatch between the reported data for the plant and the modelling which causes inaccuracies for the weighting of decision variables in the cost function.

Performance of the optimiser

The model simplification has a clear impact on the computational requirement for solving the optimisation problem as both the number of function evaluations and run time for the optimiser is significantly reduced. This was expected as the simplification reduces the number of heat exchanger calculations and removes the nested loop over HEX-8.

Restarting both problems in the identified optimal point returned the optimiser to the same point as did moving the initial starting point further away from the identified optimal point. Due to the numerical noise from the tolerances in the recycle loops the identified point is uncertain and the optimal operating point should be conceived as more of a optimal region where a small perturbation in one of the unconstrained decision variables may give a marginally better (more negative) cost function whilst a larger step again increases the cost.

5.2 Subsets 1(b) and 2(b)

The optimisation for subset 1(b) and 2(b) increases the profit by 18% and 11%, and the values for the decision variables are given in Table 5.4 and 5.5 on the next page. As for the optimisation results above the optimisation minimises the use of external cooling utilities (cooling water) and optimises the compressor operation 1(a). The main difference in the income is due to 2(b) including the cost for CW-2, the higher compressor operating point for 2(b) and the amount of produced ammonia.

The inequality in compressor operating point is that 2(b) includes the separation section for separation of liquid ammonia, which is increased with a larger degree of cooling and from a raised pressure in the separation section. The simplified model in 1(b) does not see this effect which is a weakness of the subdivision where the amount of delivered cooling does not effect the flow of ammonia to the section. This causes the optimisation to simply maximise the recovery of ammonia in the two product streams with the least possible use of compressor power. The difference in produced ammonia in the two subsets is caused by the optimal conditions for 2(b) passes more ammonia to vapour recycle and purge compared to the feed to 1(b) which is based on the nominal operating value. The two remaining unbounded variables are the split of the product vapour stream from the reactor and the speed for the air cooler AC-2. For these variables the optimal split factor (HEX-7/HEX-8) is close to the ratio found for the optimisation of subset 1(a). Similar to the results from the reaction section the air cooler has little impact on the stream temperature drop in the bounds of operation with negligible impact on the cost function.

As for the optimisations in subsets 1(a) and 2(a), we make the same observations with regards to the minimisation of utilities; one would expect the pre-cooling before the compressors to be maximum for the highest production of liquid ammonia and compressor efficiency. In the refrigeration section the nominal values for the flow of cooling water also seems excessively large.

Table 5.4: Optimisation results for Section 1(b).

Decision variable	Nominal value	Optimal value	Comment
C2 Compressor speed [rpm]	7736	7561	
CW-3 Flow rate [tonne/hr]	399.2	300.0	Lower bound
CW-4 Flow rate [tonne/hr]	1499.5	1125.0	Lower bound
AC-2 Demand Speed [rpm]	173	168.4	
Cost	-3265.7	-3656	
NH_3 [tonne/hr]	51.25	51.5	
Optimiser performance			
Function evaluations	-	350	
Run time [min]	-	3.14	

Table 5.5: Optimisation results for Section 2(b).

Decision variable	Nominal value	Optimal value	Comment
CW-2 Cooling [tonne/hr]	725.9	545.2	Lower Bound
Split HEX-8/HEX-9 [-]	0.535	0.530	
Compressor speed C2 [rpm]	7736	7683	
CW-3 Cooling [tonne/hr]	399.22	302.3	Lower Bound
CW-4 Cooling [tonne/hr]	1499.53	1127.5	Lower Bound
AC-2 Cooling [rpm]	173	127.5	
Cost	-2559.0	-3025.6	
NH_3 production [tonne/hr]	49.98	49.43	
Optimiser performance			
Optimiser performance	-	365	
Run time [min]	-	10.3	

Performance of the optimiser

The optimisation of subset 1(b) which only looks at the refrigeration section was the fastest and required the least function evaluations to find a solution as expected as it represents the smallest optimisation problem with the least number of process units and decision variables. Conversely subset 2(b) takes longer to solve as convergence of the HYSYS flowsheet takes longer time in the larger model. Both models required fewer function evaluations compared to subsets 1(a) and 2(a) due to the lower number of decision variables in the optimisation.

Both subsets converged to the same solution when started in the optimal point and further away than the initial starting point. For the optimal solution in these subsets it was also noticed that small changes in the unconstrained decision variables gave a marginal change (less than 1%) in the objective function.

5.3 Summary of optimisation results

The following key observations are made from the optimisation results in addition to the values for the decision variables in the tables:

Decision variables at bounds: The maximization of the HP-steam production was expected as it both gives income and decreases the need for cooling in the separation section, whilst the low value for the cooling water streams is counter intuitive and seems to be caused by too high cost and/or large scale of the cooling flows.

Insensitivity to unbounded decision variables: The AC coolers have little effect on the temperature drop over the unit and cost function as the temperature drop over the unit is constant except for very low fan speeds outside the lower bound of the decision variable. The purge ratios are kept close to the nominal point in the optimisation indicating these are close to optimal for heat integration.

Conflicting results from reduced models: The optimisation of the simplified model of the separation in subset 2(a) and the standalone refrigeration (1(b)) section yields conflicting results from the optimisation of the larger subsets, which seems to be caused by the reduction of interacting loops to their nominal value in the subsets. These conflicting results are the higher optimal compressor speed found for 2(a) and lower refrigeration compressor speed in 1(b).

Chapter 6

Discussion

This chapter summarises and discusses aspects with the Hysys model and the optimisation method, strategy and results. Finally the suggested further work is presented.

6.1 Aspects of the model and optimiser

The following is a recap of the issues found with the Hysys modelling and optimisation and the steps taken to mitigate these problems, other possible solutions are also discussed.

6.1.1 Modelling issues

The nominal steady state model of the ammonia plant gave an accurate picture of the plant operation which coincided with the reported plant data. However when moving too far away from the nominal point the plant model in Hysys was prone to failure caused by temperature approach in the heat exchangers and excessive pressure drop over process units causing negative pressures. This was resolved by limiting the bound for the decision parameters, especially the split ratios for stream, to ensure convergence in each flowsheet evaluation. In the optimisation the tightly bounded decision variables did not go to their constraints therefore this seems as a reasonable approach to the temperature approach issue.

With regards to the pressure drop for the heat exchangers, even with the empirical equation (3.10 on page 24), the calculated pressure drops was excessive for large flow sheet perturbations and fixed pressure drops were implemented for the exchangers. The calculation was kept in as a control to check that none of the process conditions in the optimal point would result in excessive pressure drops based on the empirical equation. The total pressure drop over all the heat exchangers was 15.1 bars with the pressure equation whilst the fixed drop was 13.3 and the small difference was deemed acceptable.

Due to the sequential modular approach to solve the flowsheet there was a lack of upstream effects from the compressors, which gives the possibility of defining the outlet pressure from the compressor without adjusting the upstream flow. This results in the apparent ability to increase the pressure excessively as there is no increased head (flow) to the compressor that reduces the compressor efficiency. Also the pressure in the recycle stream had to be fixed to C1-HP discharge pressure as discussed in Section 3.2.1 on page 22. These pressure issues caused less of a discrepancy as the optimisations tended to stay closer to the nominal value than approaching either of the bounds, but this is a mismatch between the steady-state and dynamic model and an aspect to keep in mind with compressor simulations.

The Haber-Bosch process is notorious for its temperature and pressure dependence, and the results presented in Figure 5.1 on page 43 are surprising; as one would suspect a larger temperature and pressure dependence for the reactor conversion. However, it appears that the implemented kinetic rate expression obtained from Yara in Equation 3.7 is too insensitive to temperature and pressure. A possible improvement would be to reduce the order of the rate expression and implement the normal form of the Arrhenius-equation.

6.1.2 Alternative modelling approaches

Alternative modelling approaches would have been to utilise the dynamic model for the optimisation, but it comes with the drawback of slow simulation (low real time factors[1]) and long settling times for the process due to the large equipment sizes. However the model could be used to verify the optimisation results. A 2nd approach for a steady-state model is to develop a an equation oriented model as discussed in 3.4.

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[1] The real-time factor is the ability in the simulation to accelerate the time-frame and still obtain an accurate simulation, this is low due to the size and complexity of the process flowsheet.

The choice to go for the sequential modular approach was based on several positive results for optimisation and control structure evaluation based on a modular flowsheet simulation of the process, for example on methanol synthesis in [23]. However the scale of these simulations have been on a much smaller basis (less process units and only two-three recycle blocks).

It would appear that the increase in units and especially the number of nested loops exacerbates the problems of accurately estimating the gradient with the finite-difference method in `fmincon`, and that this reduces the accuracy of the optimal solution in the optimisation. This also adds to the challenges in building a Hysys model that is stable and reaches the solution for all plant perturbations for process conditions of interest.

6.1.3 Alternative optimisation approach

As mentioned in Section 4.1 on page 29 the problem related to the inaccuracy introduced in the Hysys recycle blocks and nested loops may be avoided if the recycle problem is raised to the optimisation level and letting the optimiser solve for the recycle problem as described. However formulating the problem in this manner adds ten variables to the optimisation for each tear stream (8 components + 2 for temperature and pressure for a complete state description) and an extensive input-output structure is necessary for passing the tear stream variables between `fmincon` and the Hysys simulation flowsheet. This will greatly reduce the time spent solving the model in Hysys, but increased spreadsheet/function evaluations is required by MATLAB to solve for the expanded equality constraint set.

6.1.4 Costing

The costing is key to obtaining the right weighting for the decision variables impact on the objective function. As it has already been noted, in the Optimisation Results section, the cost for cooling water seems to be too large, resulting in minimising the use of this utility. The information for the refrigeration section compressor C2 was limited and the costing was based on the steam consumption of C1 in the lower operating range. However C2 is operated using medium pressure steam that is let down from the high pressure turbine powering C1. This gives a higher operating cost for powering C2 than what is the case for the actual plant. For more accurate costing the turbine model would have to be expanded.

Further modifications of the cost function for example penalising ammonia lost to the purge streams for the problem formulation in Equation 4.1 on page 29 may increase the production and factors in the cost for treating the purge for ammonia.

6.2 Optimisation strategy

The plant subdivision clearly reduces the computational effort with the reduction of decision variables and unit operations in each subset to a point were it can be solved with reasonable computational effort. For the plant subdivision it is important to ensure a coherent optimisation goal to avoid conflicting targets in the optimisation. This was done in the ammonia optimisations by including the ammonia production in the sets as a income.

From the optimisation it is clear that some of the interacting structure have to be kept or represented in the subdivided set to ensure that the model is representative of the full process. This became evident in the optimisation of subset 1(b) where the lack of interaction with the separation section neglected the impact of the delivered cooling on the produced amount of ammonia. This also indicates that the choice of separation is not arbitrary but should be made with the aim to keep as much as possible information within the subset. Consequently a closer study is also needed into which subdivisions and how small sets will yield an optimisation that is still valid for the full plant. The choice in this study was to separate with regards to a logical choice based on the sequential ordering of the plant units. Another could bee to separate out a element that sits inside the other sections for example the reaction section and optimise this for maximal production of ammonia and then maximise the other sections around this in a hierarchical manner. However this might not ensure the most profitable plant operation mode, if the costs are too high in the other units supporting the optimal operation of the reaction section.

The optimisation of one subunit will disturb the input to the other units and a framework for passing information between the optimised subsets is necessary as the new optimal settings will disturb the input to the other sections. These have been kept at the nominal value for all of the optimisations in this study and this may effect the validity of the optimal points found by the optimiser.

Identifying the optimal steady-state operating point may be one of the most time-consuming tasks in control-structure design and solving the problem in a more effective manner is of major benefit to the control system engineer [27]. A plant separation strategy may be a possible technique for solving the optimisation problem of complex coupled plants, as smaller sub-problems that are easier to define and requires less computational effort. The results in this thesis indicate that the plant separation may be a viable approach for optimisation but more work is required to verify and develop the strategy especially with regards to the choice of separation.

6.3 Future work

Suggested further work for the optimisation of the ammonia plant and developing the optimisation strategy is outlined below:

Pressure Description Better description of pressure drops for process units and the upstream effect of the compressor for a more accurate description of the compressor pressure and flow effect.

Cost function Obtaining a better description for the refrigeration section turbine steam consumption related to the production of MP-steam for the high pressure turbine. Include purge costs in the problem formulation for a more correct weighting of the decision variables

Connection between subsets Implement disturbances and a method for passing information between the optimised subsets, instead of relying on the nominal conditions for the optimisation of each subset.

Let `fmincon` solve for recycle blocks Implementing the tear streams as constraints in the optimiser and assess this method performance on the nested loops with the aim of reducing noise from recycle loop tolerances.

Develop separation strategy Verify and develop the separation strategy with regards to how to separate the process model and for which separations and conditions the strategy is valid.

Chapter 7

Conclusion

The optimisation is successful in increasing the plant profitability in all the plant sections for the given conditions. This is achieved by minimising the use of cooling utilities, maximising the high pressure steam production and optimising the compressor operation, split ratios and air cooling in the relevant sections. The division strategy is successful in reducing the computational effort for the optimisation, as fewer unit operations and decision variables have to be considered in each subset. Care has to be taken in the formulation of the cost function and selection of divided sets to avoid conflicting optimisation objectives; each subdivision has to retain enough process information to avoid diverging optimisation results.

Due to the model limitations in the steady state modular simulation of the plant in HYSYS, the optimisation is performed on a limited window of process variables and the results would have to be verified by dynamic simulation and and careful evaluation for practical implementation.

More work is required to determine the best way of dividing and representing the partitioned plant, how to pass information between the optimised sets for a coherent optimisation and how to handle disturbances, especially disturbances in the feed stream.

Bibliography

[1] Appl, M. [2006], 'Ammonia, 2. production processes', *Ullmann's Encyclopedia of Industrial Chemistry* .

[2] Aspentech [2005*a*], Hysys $^{®}$ 2004.2 customization 0guide, Technical report.
URL: *https://www.ualberta.ca/CMENG/che312/F06ChE416/HysysDocs/AspenHYSYSCustomizationGuide.pdf*

[3] Aspentech [2005*b*], Hysys$^{®}$ 2004.2 operations guide, Technical report.
URL: *https://www.ualberta.ca/CMENG/che312/F06ChE416/HysysDocs/AspenHYSYSOperationsGuide.pdf*

[4] Aspentech [2005*c*], Hysys$^{®}$ 2004.2 simulation basis, Technical report.
URL: *https://www.ualberta.ca/CMENG/che312/F06ChE416/HysysDocs/AspenHYSYSSimulationBasis.pdf*

[5] Atkins, P. and De Paula, J. [2002], *Atkins' Physical Chemistry*, number v. 1, Oxford University Press.

[6] *Best Available Techniques for Pollution Prevention and Control in the European Fertilizer Industry* [2000], Technical report, European Fertilizer Manufacturers' Association.

[7] Biegler, L. T. [2010], *Nonlinear Programming: Concepts, Algorithms, and Applications to Chemical Processes*, MOS-SIAM Series on Optimization, Society for Industrial and Applied Mathematics, SIAM.

[8] Biegler, L. T., dong Lang, Y. and Lin, W. [2014], ‘Multi-scale optimization for process systems engineering’, *Computers & Chemical Engineering* **6**0(0), 17 – 30.

[9] Biegler, L. T., Grossmann, I. and Westerberg, A. [1997], *Systematic methods of chemical process design*, Prentice-Hall international series in the physical and chemical engineering sciences, Prentice Hall PTR.

[10] Biegler, L. T. and Hughes, R. [1982], ‘Infeasible path optimization with sequential modular simulators’, *AIChE journal* **2**8(6), 994–1002.

[11] Biegler, L. T. et al. [1987], ‘Process flowsheet optimization: recent results and future directions’.
URL: *http://repository.cmu.edu/cgi/viewcontent.cgi?article=1122&context=cheme*

[12] Caballero, J. A. and Grossmann, I. E. [2008], ‘An algorithm for the use of surrogate models in modular flowsheet optimization’, *AIChE Journal* **5**4(10), 2633–2650.

[13] *Current world fertilizer trends and outlook to 2018* [2015], Technical report, Food and Agriculture Organization of the United Nations.

[14] Fogler, H. [2006], *Elements of Chemical Reaction Engineering*, Elements of Chemical Reaction Engineering, Prentice Hall PTR.

[15] Froment, G. and Bischoff, K. [1979], *Chemical reactor analysis and design*, Wiley.

[16] Gaines, L. D. and Gaddy, J. L. [1976], ‘Process optimization by flow sheet simulation’, *Industrial & Engineering Chemistry Process Design and Development* **1**5(1), 206–211.

[17] Gillespie, L. J. and Beattie, J. A. [1930], ‘The thermodynamic treatment of chemical equilibria in systems composed of real gases. i. an approximate equation for the mass action function applied to the existing data on the haber equilibrium’, *Phys. Rev.* **3**6, 743–753.

[18] Haber, F. and Le Rossignol, R. [1907], ‘Über das ammoniakgleichgewicht’, *Berichte der deutschen chemischen Gesellschaft* **4**0(2), 2144–2154.

[19] Hager, T. [2008], *The Alchemy of Air*, Crown/Archetype.

[20] Jennings, J. [2013], *Catalytic Ammonia Synthesis: Fundamentals and Practice*, Fundamental and Applied Catalysis, Springer US.

[21] Júlio, A. D. C. [n.d.], Comparison of chemical process simulators: Aspen vs. hysys, Technical report, Instituto Superior Técnico, Lisboa, Portugal.
URL: *https://fenix.tecnico.ulisboa.pt/downloadFile/395137861652/*

[22] Kreyszig, E. [2010], *Advanced Engineering Mathematics*, John Wiley & Sons.

[23] Lúa, A. R. [2014], Economic plantwide control for a methanol plant using commerical process simulation software, Master's thesis, NTNU.

[24] Mathworks [2015*a*], Choosing a solver, Technical report. Acessed 06.07.2015.
URL: *http://se.mathworks.com/help/optim/ug/choosing-a-solver.html*

[25] Mathworks [2015*b*], *fmincon*, find minimum of constrained nonlinear multivariable function, Technical report. Acessed 06.07.2015.
URL: *http://se.mathworks.com/help/optim/ug/fmincon.html*

[26] Skogestad, S. [2003], *Prosessteknikk, Masse- og energibalanser*, 2 edn, Tapir Akademiske Forlag.

[27] Skogestad, S. [2012], Economic plantwide control, *in* G. Rangaiah and V. Kariwala, eds, 'Plantwide Control: Recent Developments and Applications', Wiley, pp. 229–251.

[28] Skogestad, S. and Postlethwaite, I. [2005], *Multivariable Feedback Control*, 2 edn, Wiley.

[29] Towler, G. and Sinnott, R. [2013], *Chemical Engineering Design: Principles, Practice, and Economics of Plant and Process Design*, Butterworth Heinemann, Butterworth-Heinemann.

Appendix A

Upstream Syngas Processing

The ammonia syngas is typically prepared via a gasification of light hydrocarbons (less than 12 C-atoms) following Equations A.1 and A.2.

$$[CH_{\boldsymbol{n}}] + H_2O \rightleftharpoons CO + H_2 + \tfrac{\boldsymbol{n}}{\boldsymbol{2}}H_2 \tag{A.1}$$

$$[CH_{\boldsymbol{n}}] + \tfrac{\boldsymbol{1}}{\boldsymbol{2}}O_2 \rightleftharpoons CO + \tfrac{\boldsymbol{n}}{\boldsymbol{2}}H_2 \tag{A.2}$$

Methane is the preferred feedstock to the gasification process as it gives the highest hydrogen to carbon ratio. Heavier hydrocarbon sources such as coal and heavy oil may also be used with partial oxidation prior to gasification. However this process is much more energy demanding due to the higher carbon ratio and 77% of all ammonia production worldwide is based on a natural gas feedstock [1].

Any oxygen containing components must be removed from the feed stream as they oxidise the catalyst in the ammonia reactor reducing the plant running time between catalyst regeneration cycles. CO from the gasification reactions is removed via the water gas shift reaction which also increases hydrogen yield as shown in Equation A.3.

$$CO + H_2O = CO_2 + H_2 \tag{A.3}$$

CO_2, H_2S and any remaining CO have to be removed from the feed stream typically by scrubbing with a suitable absorbent. Remaining H_2O and CO_2

is removed by washing the fresh syngas feed with liquid NH_3 from the outlet NH_3-product stream. Other more severe catalyst poisons include sulphur, phosphor, arsenic and chlorine containing compounds. These are removed upstream of syngas preparation.

A.1 Disturbances originating in syngas production

The main disturbance originating from the synthesis gas preparation is the molar flow and composition (the H_2:N_2 ratio) due to varying composition in the delivered natural gas to the plant. This may have a major impact on the reaction and stream composition in the ammonia plant as the syngas composition has a major impact on the recycle syngas composition and the ideal reactor operating conditions [1]. Other disturbances such as temperature and pressure are neglected as we can imagine rejecting these with the existing plant control in the make up section.

More details on the upstream syngas processing is available in Chapter 6.1 Syngas Production of [1].

Appendix B

Nominal Process Conditions

The following contains data for the nominal conditions for each plant section in the studied ammonia plant. A molar flows are relative to the reaction section feed stream.

B.1 Syngas makeup

Table B.1: Nominal molar composition and flows in the syngas makeup section.

Component	Feed	NH3 Wash	Recycle	Feed Reaction
Hydrogen	0.74	0.00	0.64	0.66
Ammonia	0.00	0.99	0.03	0.02
Helium	0.00	0.00	0.01	0.01
Argon	0.00	0.00	0.07	0.06
Nitrogen	0.25	0.00	0.20	0.21
H2O	0.00	0.00	0.00	0.00
Methane	0.01	0.01	0.05	0.04
Oxygen	0.00	0.00	0.00	0.00
T [c]	7.49	-17.14	25.93	51.70
P [barg]	26.34	127.30	127.00	139.49
Flow [mol%]	0.21	0.00	0.78	1.00

B.2 Reaction section

Figure B.1 shows the nominal conditions of the reactor profile. From the figure it is clear that the reactor is approaching equilibrium at the outlet of the second bed, and due to the formation of ammonia the reaction rate does not increase with the temperature increase. The nominal composition for the reaction section is in Table B.2.

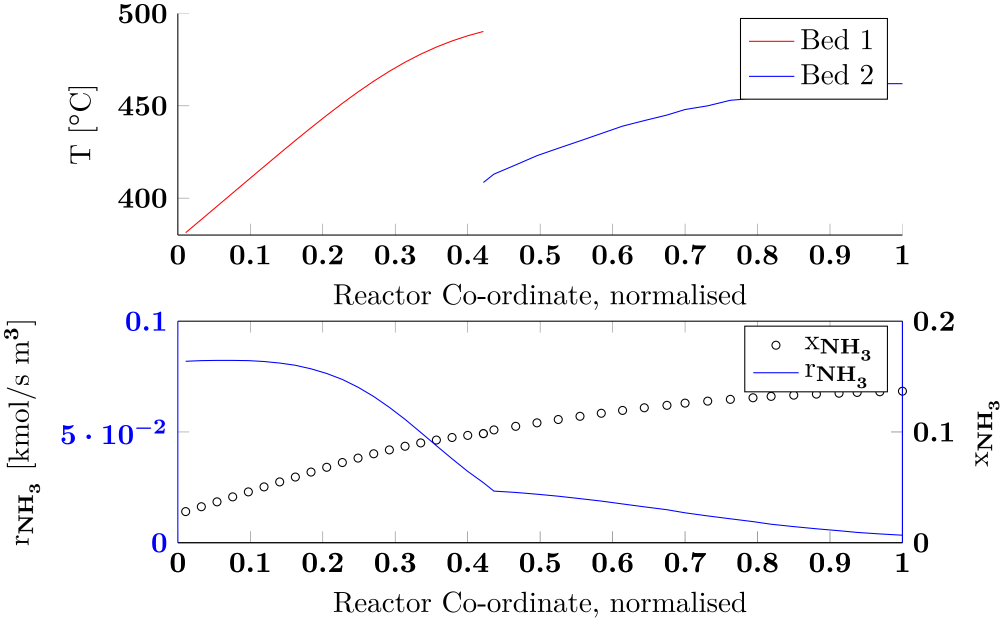


Figure B.1: Reactor temperature and reaction profile for nomnial conditions.

Table B.2: Nominal molar compositions and flows in the reaction section.

Component	Feed PFR-1	Feed PFR-2	Feed HEX-3	Separation feed
Hydrogen	0.66	0.60	0.57	0.57
Ammonia	0.02	0.10	0.14	0.14
Helium	0.01	0.01	0.01	0.01
Argon	0.06	0.06	0.06	0.06
Nitrogen	0.21	0.19	0.18	0.18
H2O	0.00	0.00	0.00	0.00
Methane	0.04	0.05	0.05	0.05
Oxygen	0.00	0.00	0.00	0.00
T [°C]	374.06	408.48	462.00	53.72
P [barg]	137.4	136.6	136.3	130.8
Flow [mol%]	1.00	0.93	0.90	0.90

B.3 Separation section

The nominal values for the flows in the separation section are given in Table B.3

Table B.3: Nominal molar compositions and flows in the separation section.

Component	Feed HEX-7	Exit HEX-8	Recirc	Feed S-4
Hydrogen	0.57	0.57	0.64	0.64
Ammonia	0.14	0.14	0.03	0.03
Helium	0.01	0.01	0.01	0.01
Argon	0.06	0.06	0.07	0.07
Nitrogen	0.18	0.18	0.20	0.20
H2O	0.00	0.00	0.00	0.00
Methane	0.05	0.05	0.05	0.05
Oxygen	0.00	0.00	0.00	0.00
T [°C]	28.67	3.41	-17.18	-14.66
P [barg]	130.0	129.1	127.4	14.7
Flow [mol%]	0.42	0.48	0.80	0.10

B.4 Refrigeration section

Nominal conditions for the refrigeration section are given in Table B.4 with data for the ammonia refrigeration coolers in Tables B.5 and B.6.

Table B.4: Nominal molar composition and flow in the refrigeration section.

Component	Feed S-5	Produced NH3	Purge VLV–12	Vapor S-8
Hydrogen	0.00	0.00	0.03	0.01
Ammonia	1.00	1.00	0.32	0.68
Helium	0.00	0.00	0.01	0.00
Argon	0.00	0.00	0.03	0.01
Nitrogen	0.00	0.00	0.02	0.01
H2O	0.00	0.00	0.00	0.00
Methane	0.00	0.00	0.60	0.28
Oxygen	0.00	0.00	0.00	0.00
T [c]	-29.30	-29.87	-29.30	21.64
P [barg]	0.27	0.16	0.27	12.80
Flow [mol%]	0.10	0.10	0.10	0.00

Table B.5: Nominal conditions in the refrigeration section for HEX-1 and HEX-5.

Component	HEX-1 NH3 Inlet/Outlet	HEX-1 Gas Inlet/Outlet	HEX-5 NH3 Inlet/Outlet	HEX-5 Gas Inlet/Outlet
Hydrogen	0.00	0.74	0.00	0.57
Ammonia	1.00	0.00	1.00	0.14
Helium	0.00	0.00	0.00	0.01
Argon	0.00	0.00	0.00	0.06
Nitrogen	0.00	0.25	0.00	0.18
H2O	0.00	0.00	0.00	0.00
Methane	0.00	0.01	0.00	0.05
Oxygen	0.00	0.00	0.00	0.00
Vapour Frac.	0.020/0.15	1.00/1.00	0.00/0.13	0.98/0.93
T [c]	5.44/5.54	18.66/7.41	11.75/12.50	28.74/13.52
P [barg]	4.2	65.3/65.0	5.66/5.66	129.8/129.2
Flow [mol%]	0.03	0.21	0.20	0.42

Table B.6: Nominal conditions in the refrigeration section for HEX-6 and HEX-7.

Component	HEX-6 NH3 Inlet/Outlet	HEX-6 Gas Inlet/Outlet	HEX-7 NH3 Inlet/Outlet	HEX-7 Gas Inlet/Outlet
Hydrogen	0.00	0.00	0.00	0.57
Ammonia	1.00	1.00	1.00	0.14
Helium	0.00	0.00	0.00	0.01
Argon	0.00	0.00	0.00	0.06
Nitrogen	0.00	0.00	0.00	0.18
H2O	0.00	0.00	0.00	0.00
Methane	0.00	0.00	0.00	0.05
Oxygen	0.00	0.00	0.00	0.00
Vapour Frac.	0.00/0.13	0.93/0.90	0.00-0.59	0.91/0.89
T [c]	-6.90/-6.33/	13.52/-3.57	-30.74/-28.74	0.26/-17.14
P [barg]	5.66-5.66	129.8/129.4	0.21/0.21	128.76/127.39
Flow [mol%]	0.20	0.42	0.07	0.90

Appendix C

Compressor Description

The following appendix gives a short description of the two compressor trains in the syngas make-up and refrigeration section of the NH_3-plant. Both compressor trains are reciprocal using steam turbines for power delivery.

C.1 Syngas compressors

The syngas compression train in the make-up section fulfils three roles:

1. Compression of the fresh syngas to the wash loop pressure so that the liquid NH_3 condensates in the wash tank, S-2.
2. Compression of the dry syngas to the recycle gas pressure over C1-HP
3. Compress the total gas feed to the reaction section pressure to make up for the pressure drop over reaction and separation section.

The characteristic curves used for defining the compressor operation are available in Figure C.2. Compressor C1-HP gives the greatest pressure increase (nominally 60 bar) whilst C1-BP consumes the most power due to the compression at elevated temperatures.

C.2 Refrigeration compressors

In the refrigeration section the compressor train pressurises the vapor stream, mainly ammonia, in the cooling cycle. The temperature increase over each compressor unit is such that the cooling is operated counter-currently from the separation section, where the last stream with the highest temperature is used for cooling the warm reactor product stream as it enters the separation section in HEX-5. The characteristic curves used for modelling the compressor in Hysys is available in Figure C.3.

C.3 Compressor turbine

The compressor turbines are powered by high pressure steam and the power delivery to the turbines is controlled by two factors: the flow of high pressure (HP-)steam through the turbine and the let down of high pressure steam to medium and low pressure (MP/LP-)steam through control valves prior to expansion in the turbine. This means that for a certain flow of high pressure steam there is a range of compressor power depending on the throttling of HP-steam to MP and LP. For steam consumption calculations it is assumed that as little as possible steam is let down meaning that turbine is operated at minimum steam consumption. There was assumed no loss of work in the coupling from the turbine to the compressor.

Figure C.1 show the steam consumption as function of total compressor power for compressor C-1 and C-2 in the range of interest for the optimisation. The discontinuities in the curves are due to intermediate flow control valves being set to full-open and the next stage valve opening. Only data for the turbine powering C-1 were available and the C-2 calculation was based on the data from C-1. The consumed amount of steam was based on a 2nd order polynomial for quick calculation in the cost function, with one polynomial for each of the four operating ranges (kinks in the curve). The correct polynomial for the operating range was selected using a logic structure in the cost function and the data were only interpolated.

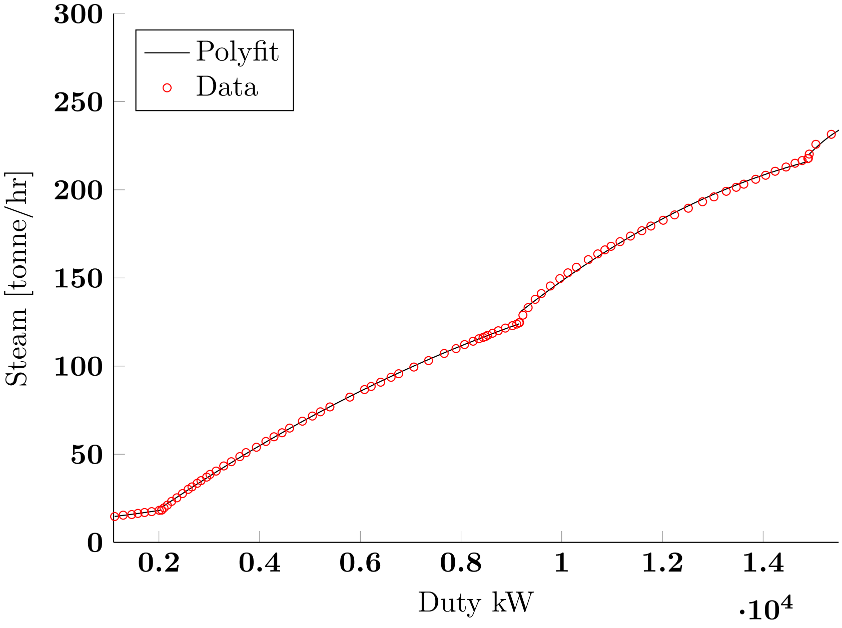
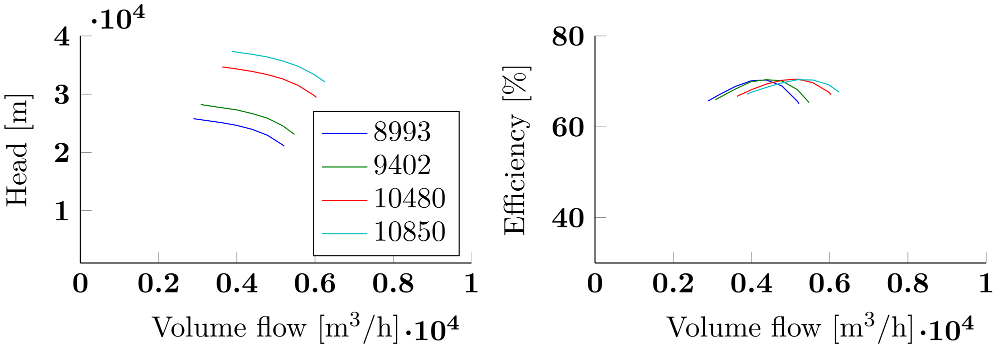
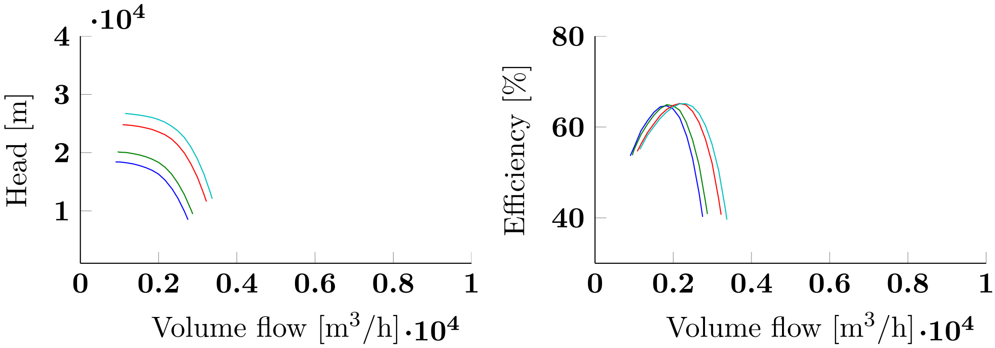


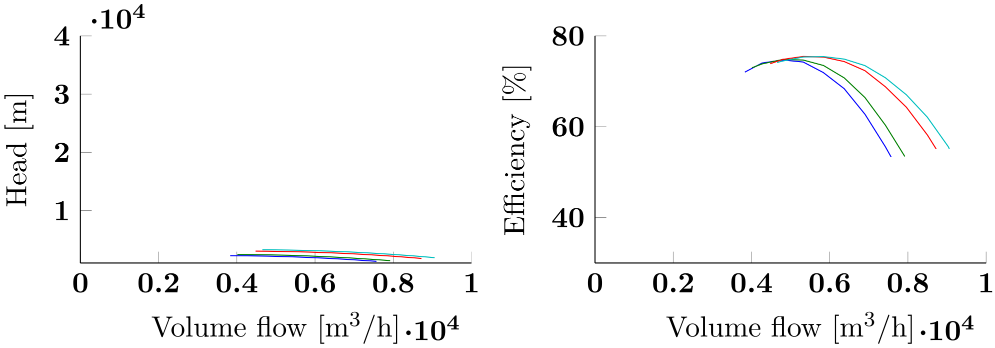
Figure C.1: Turbine steam consumption for demanded power from compressor C-1 and C-2.



(a) C1-BP

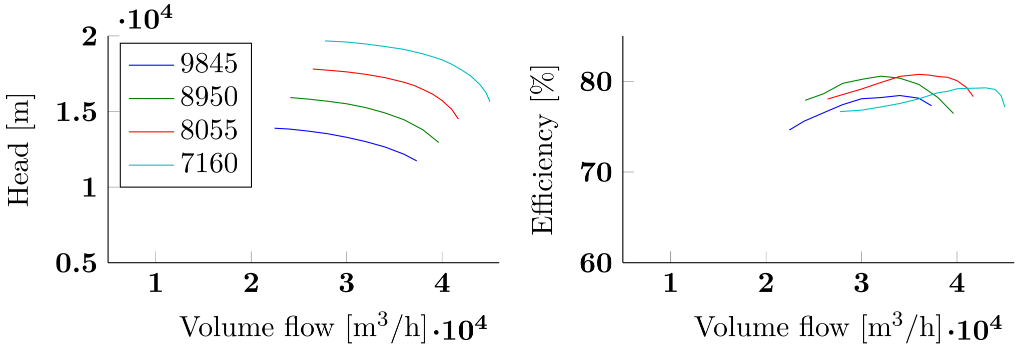


(b) C1-HP

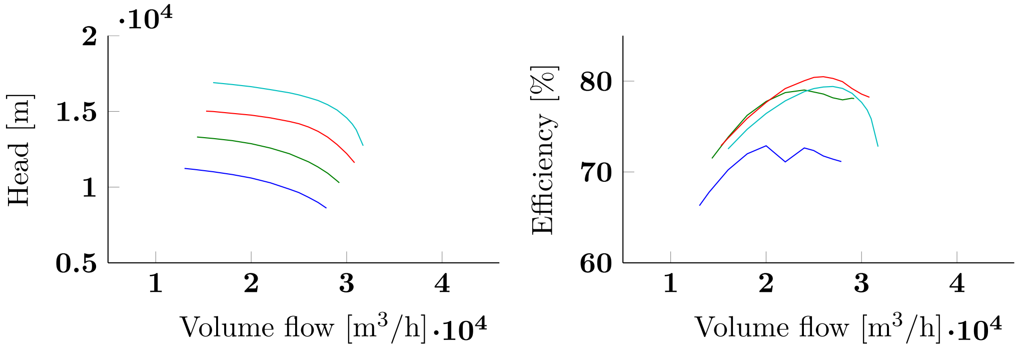


(c) C1-RE

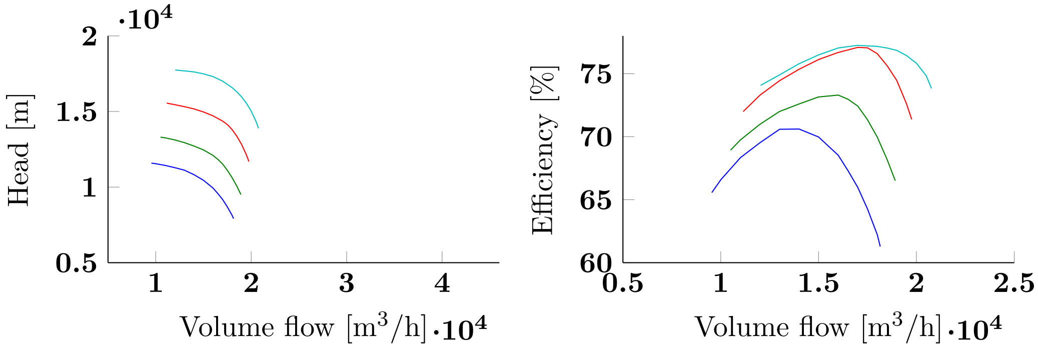
Figure C.2: Compressor C1 characteristic curves at various compressor speeds, the legend is for the compressor speed in RPM.



(a) C2-1



(b) C2-2



(c) C2-2

Figure C.3: Compressor C2 characteristic curves at various compressor speeds, the legend is for the compressor speed in RPM.

Appendix D

MATLAB Code

This section provides the MATLAB code used in the optimisation

D.1 Non-linear optimiser *fmincon*

The following code attaches to the open HYSYS flowsheet and applies the *fmincon* optimisation routine:

```
%Non—linear optimisation w. fmincon
%This optimisation routine grabs the open HYSYS file and applies the
%fmincon optimiser to the flowsheet
%In this case: Subset 1a Reaction Section

%Grabbing Hysys object
    global hy,global hycase
    hy=actxserver('Hysys.Application'); %Hysys handle w. actx
    hycase=hy.Activedocument;
%Initial inputs, u0 is vector containing initial HYSYS—inputs
    isprd=hyspread(hy,'Input');
   %u0=[CW—1,C1—RPM,Split VLV—2,HP—S,AC—1,CW—2,Purge]
    u0=hyvalue(hycell(isprd,{'D2','D3','D4','D5','D6','D7','D8','D9'}));
%Define bounds for input (for MATLAB optimization)
    global lb, global ub
    %Lower bounds
    lb=hyvalue(hycell(isprd,{'E2','E3','E4','E5','E6','E7','E8','E9'}));
    %Upper bounds
    ub=hyvalue(hycell(isprd,{'F2','F3','F4','F5','F6','F7','F8','F9'}));
%Nonlinear optimisation w. fmincon
```

```
    %Scale inputs to bounds
    u0s=uscale(u0,lb,ub);
    %Input bounds for optimization
    lbm=zeros(size(lb));
    ubm=ones(size(ub));
    opt=optimset('TolFun',9e-8,...
                 'TolCon',1e-4,...
                 'Display','iter',...
                 'Algorithm','interior-point',...
                 'Diagnostics','on',...
                 'FinDiffType','central',...
                 'ScaleProblem','obj-and-constr',...
                 'FinDiffRelStep',1e-2);




    tic
    [x,fval,exitflag,output,lambda]=fmincon(@(u)objfunct(u),u0s,[],[],[]...
                                   ,[],lbm,ubm,@(u)constraints(u),opt);
    elapsed_time=toc;
```

D.2 Objective function

The following function descales the input from the *fmincon* optimiser and passes it to the HYSYS flowsheet, holds the optimiser whilst HYSYS solves for the new input and calculates a new cost that is passed back to the optimiser.

```
function c=objfunct(u)
global hy,global hycase,global lb, global ub
%(de)Scale input from MATLAB (0-1) to HYSYS bounded values
    u=udescale(u,lb,ub);
%Connection to HYSYS spreadsheet 'Input' to give newinput u
    usprd=hyspread(hy,'Input');
    uc=hycell(usprd,{'B2','B3','B4','B5','B6','B7','B8','B9'});
%Set HYSYS solver on hold,pass new input, activate solver
    hycase.solver.CanSolve=0;
    hyset(uc,u)
    hycase.solver.CanSolve=1;
%Solve for new input
    while hycase.Solver.issolving~=0
    %Do nothing
    end
%Connect to Hysys spreadsheet 'CostFunc' for cost c
    csprd=hyspread(hy,'CostFunc');
```

```
    c=hyvalue(hycell(csprd, {'A2'}));
end
```

D.3 Contraints

The following function descales and passes the new input to HYSYS from the *fmincon* optimiser to check that the input satisfies the constraints

```
function [c,ceq] = constraints(u)
%Constraints Function to pass inequality c and equality constraints ceq
%from HYSYS to MATLAB solver fmincon
global hy, global hycase, global lb, global ub
%(de)Scale input from MATLAB (0—1) to HYSYS bounded values
    u=udescale(u,lb,ub);
%Connection to HYSYS spreadsheet 'Input' for input u
    usprd=hyspread(hy,'Input');
    uc=hycell(usprd,{'B2','B3','B4','B5','B6','B7','B8','B9'});
%Set HYSYS solver on hold,pass new input, activate solver
    hycase.solver.CanSolve=0;
    hyset(uc,u)
    hycase.solver.CanSolve=1;
%Solve for new input
    while hycase.Solver.issolving
    %Do nothing
    end
%Connection to HYSYS spreadsheet 'Constraints'
    consprd=hyspread(hy,'Constraints');
    c=hyvalue(hycell(consprd,{'A8','A9','A10','A11'}));
    ceq=[];%hyvalue(hycell(consprd,{'A2','A5'}));
end
```

D.4 HYSYS connectivity

The following functions are used for creating the MATLAB connection to the necessary spreadsheets for passing inputs and output. These have been created by PhD Olaf Trygve Berglihn, see code for more information.

```
function CellValue = hyvalue(CellObject)
% HYVALUE Returns the value of a Hysys spreadsheet cell.
%    hyvalue(CellObject) — CellObject can be a single object or a cell
%    array of objects.
%
%    Copyright (C) 1999 Olaf Trygve Berglihn <olafb@pvv.org>
%    Please read the files license.txt and lgpl.txt
```

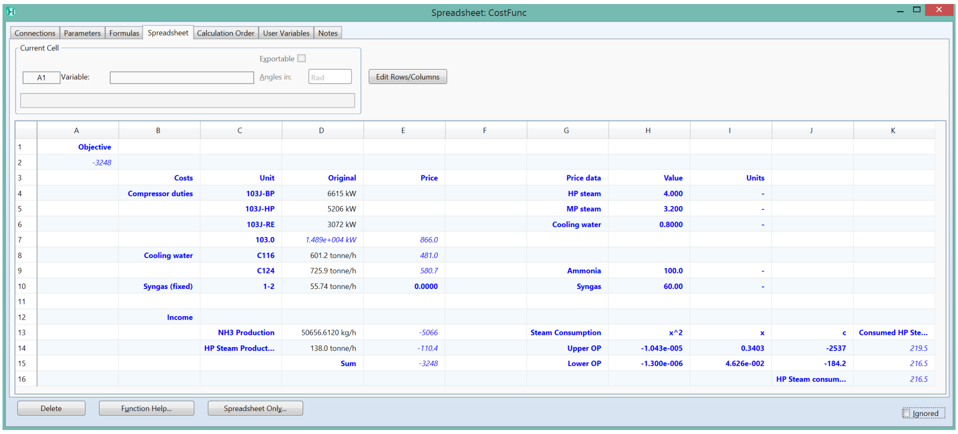
```
%% $Id: hyvalue.m,v 1.5 1999/04/20 08:52:54 olafb Exp $
%% ——————————
%% Changelog:
%%
%% $Log: hyvalue.m,v $
%% Revision 1.5  1999/04/20 08:52:54  olafb
%% The library is now under LGPL license.
%%
%% Revision 1.4  1999/04/18 14:04:44  olafb
%% Added support for cell matrises of activeX—objects.
%%
%% Revision 1.3  1999/04/18 13:54:12  olafb
%% hysyslib/
%%
%% Revision 1.2  1999/04/16 08:38:16  olafb
%% Added support for cell arrays of aciveX objects
%%
%% Revision 1.1  1999/04/07 12:03:37  olafb
%% Initial revision
%%

if isa(CellObject, 'cell')
  for n1 = 1:size(CellObject,1)
    for n2 = 1:size(CellObject,2)
%      if isa(CellObject{n1,n2}, 'activex')
    CellValue(n1,n2) = CellObject{n1,n2}.CellValue;
%      end
    end
  end
else
  CellValue = CellObject.CellValue;
end



function SpreadsheetObject = hyspread(ApplicationObject, SpreadsheetNameString)
% HYSPREAD Returns the activeX object for a spreadsheet in Hysys
%     hyspread(ApplicationObject, SpreadsheetNameString)
%
%    Copyright (C) 1999 Olaf Trygve Berglihn <olafb@pvv.org>
%    Please read the files license.txt and lgpl.txt

%% $Id: hyspread.m,v 1.2 1999/04/20 08:52:53 olafb Exp $
%% ——————————
%% Changelog:
%%
%% $Log: hyspread.m,v $
%% Revision 1.2  1999/04/20 08:52:53  olafb
%% The library is now under LGPL license.
```

```
%%
%% Revision 1.1  1999/04/07 12:01:39  olafb
%% Initial revision
%%
%%


SpreadsheetObject = get ...
                    (ApplicationObject.ActiveDocument.Flowsheet.Operations,..
                     'Item', SpreadsheetNameString);


function CellObject = hycell(SpreadsheetObject, CellNameString)
% HYCELL Returns the column cell array of activeX objects of cells in Hysys.
%    hycell(SpreadsheetObject, CellNameString) returns the object for the
%    cell name given by CellNameString. CellNameString may be a cell array.
%
%    Copyright (C) 1999 Olaf Trygve Berglihn <olafb@pvv.org>
%    Please read the files license.txt and lgpl.txt

%% $Id: hycell.m,v 1.5 1999/04/20 08:52:52 olafb Exp $
%% ------------
%% Change log:
%%
%% $Log: hycell.m,v $
%% Revision 1.5  1999/04/20 08:52:52  olafb
%% The library is now under LGPL license.
%%
%% Revision 1.4  1999/04/18 13:54:11  olafb
%% hysyslib/
%%
%% Revision 1.3  1999/04/16 08:38:16  olafb
%% Added support for cell arrays of aciveX objects
%%
%% Revision 1.2  1999/04/07 11:56:43  olafb
%% *** empty log message ***
%%

CellObject = {};

if isa(CellNameString, 'cell')
  for n1 = 1:size(CellNameString,1)
    for n2 = 1:size(CellNameString,2)
    CellObject{n1,n2} = get (SpreadsheetObject, 'Cell', CellNameString{n1,n2}
    end
  end
else
  CellObject{1} = get (SpreadsheetObject, 'Cell', CellNameString);
end
```

Appendix E

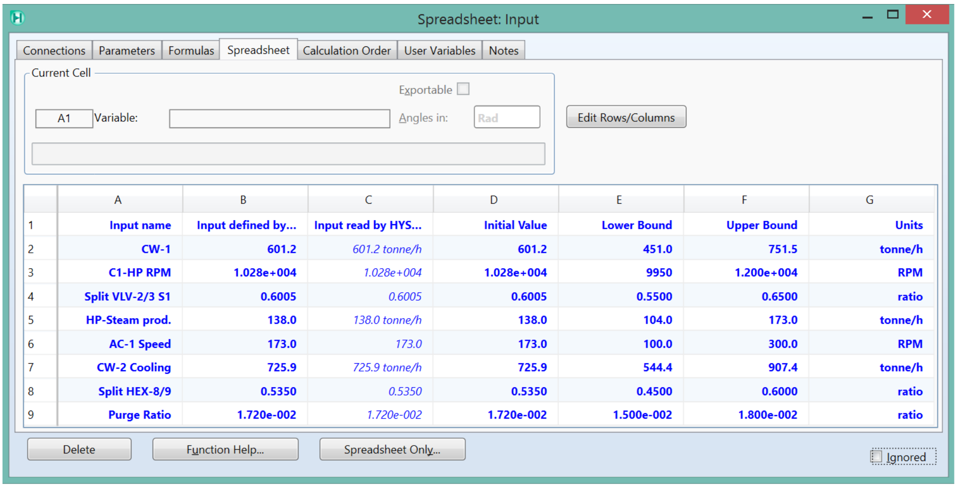
HYSYS Settings

The following are examples of the HYSYS spreadsheets, Cost Function, Inout and Constraints described in section 4.5.



	A	B	C	D	E	F	G	H	I	J	K
1	**Objective**										
2	*-3248*										
3		**Costs**	**Unit**	**Original**	**Price**		**Price data**	**Value**	**Units**		
4		**Compressor duties**	**103J-BP**	6615 kW			**HP steam**	**4.000**	**-**		
5			**103J-HP**	5206 kW			**MP steam**	**3.200**	**-**		
6			**103J-RE**	3072 kW			**Cooling water**	**0.8000**	**-**		
7			**103.0**	*1.489e+004 kW*	*866.0*						
8		**Cooling water**	**C116**	601.2 tonne/h	*481.0*						
9			**C124**	725.9 tonne/h	*580.7*		**Ammonia**	**100.0**	**-**		
10		**Syngas (fixed)**	**1-2**	55.74 tonne/h	**0.0000**		**Syngas**	**60.00**	**-**		
11											
12		**Income**									
13			**NH3 Production**	50656.6120 kg/h	*-5066*		**Steam Consumption**	**x^2**	**x**	**c**	**Consumed HP Ste...**
14			**HP Steam Product...**	138.0 tonne/h	*-110.4*		**Upper OP**	**-1.043e-005**	**0.3403**	**-2537**	*219.5*
15				**Sum**	*-3248*		**Lower OP**	**-1.300e-006**	**4.626e-002**	**-184.2**	*216.5*
16										**HP Steam consum...**	*216.5*

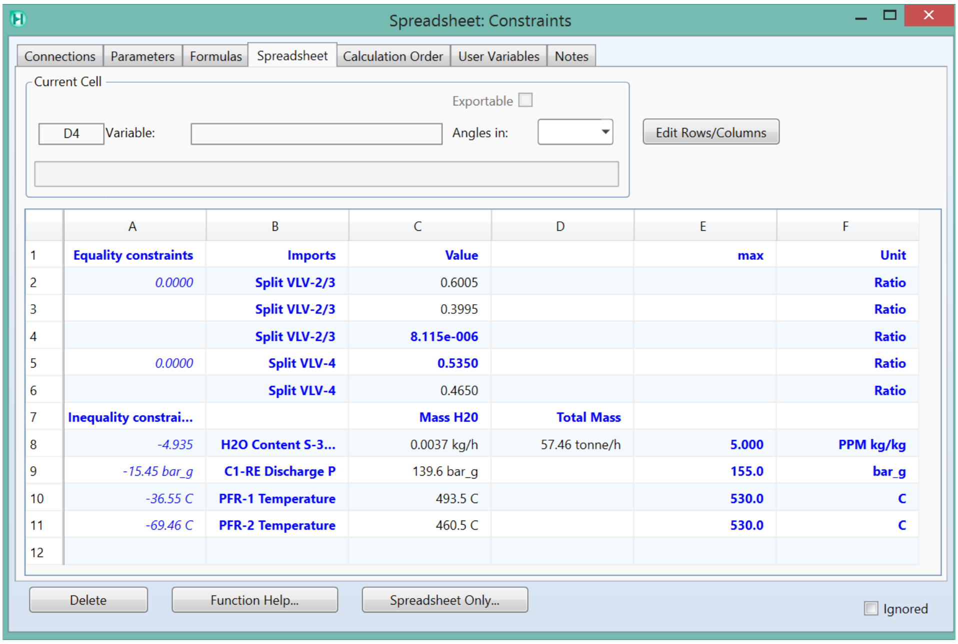
Figure E.1: The HYSYS input spreadsheet for passing the value of the cost function to the *fmincon* optimisation routine from the simulation environment



A1 Variable:

	A	B	C	D	E	F	G
1	**Input name**	**Input defined by...**	**Input read by HYS...**	**Initial Value**	**Lower Bound**	**Upper Bound**	**Units**
2	**CW-1**	**601.2**	*601.2 tonne/h*	**601.2**	**451.0**	**751.5**	**tonne/h**
3	**C1-HP RPM**	**1.028e+004**	*1.028e+004*	**1.028e+004**	**9950**	**1.200e+004**	**RPM**
4	**Split VLV-2/3 S1**	**0.6005**	*0.6005*	**0.6005**	**0.5500**	**0.6500**	**ratio**
5	**HP-Steam prod.**	**138.0**	*138.0 tonne/h*	**138.0**	**104.0**	**173.0**	**tonne/h**
6	**AC-1 Speed**	**173.0**	*173.0*	**173.0**	**100.0**	**300.0**	**RPM**
7	**CW-2 Cooling**	**725.9**	*725.9 tonne/h*	**725.9**	**544.4**	**907.4**	**tonne/h**
8	**Split HEX-8/9**	**0.5350**	*0.5350*	**0.5350**	**0.4500**	**0.6000**	**ratio**
9	**Purge Ratio**	**1.720e-002**	*1.720e-002*	**1.720e-002**	**1.500e-002**	**1.800e-002**	**ratio**

Figure E.2: The HYSYS input spreadsheet for passing decision variables from MATLAB *fmincon* optimisation routine to the simulation environment



D4 Variable:

	A	B	C	D	E	F
1	**Equality constraints**	**Imports**	**Value**		**max**	**Unit**
2	*0.0000*	**Split VLV-2/3**	0.6005			**Ratio**
3		**Split VLV-2/3**	0.3995			**Ratio**
4		**Split VLV-2/3**	**8.115e-006**			**Ratio**
5	*0.0000*	**Split VLV-4**	**0.5350**			**Ratio**
6		**Split VLV-4**	0.4650			**Ratio**
7	**Inequality constrai...**		**Mass H20**	**Total Mass**		
8	*-4.935*	**H2O Content S-3...**	0.0037 kg/h	57.46 tonne/h	**5.000**	**PPM kg/kg**
9	*-15.45 bar_g*	**C1-RE Discharge P**	139.6 bar_g		**155.0**	**bar_g**
10	*-36.55 C*	**PFR-1 Temperature**	493.5 C		**530.0**	**C**
11	*-69.46 C*	**PFR-2 Temperature**	460.5 C		**530.0**	**C**
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Figure E.3: The HYSYS input spreadsheet for evaluating the contraints satisfactions for the MATLAB inputs to HYSYS