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EXECUTIVE SUMMARY OF THE THESIS

Dynamics and Control of a Load Flexible Green Ammonia Plant

LAUREA MAGISTRALE IN CHEMICAL ENGINEERING - INGEGNERIA CHIMICA

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1. Introduction

With the growing concern over climate change, innovative low-carbon solutions such as green ammonia have gained particular interest. Currently, ammonia production accounts for 1.8% of the global CO_2 emissions [1]. Both to align the sustainable development scenario and to reach net zero by 2050 this number needs to be reduced significantly, as demonstrated by Figure 1, where the International Energy Agency (IEA) predictions are reported.
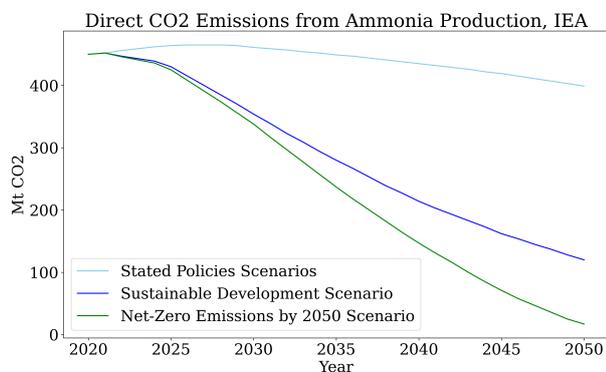

Figure 1: Direct CO_2 emissions from ammonia production, 2020-2050, International Energy Agency [1].

Green ammonia, produced from green hydro-gen, could be a solution to reduce these emissions. Currently, the vast majority of ammonia is produced from hydrogen obtained through methane reforming, a highly carbon-intensive process. Replacing this hydrogen with green hydrogen, produced through water electrolysis powered by renewable energy, will greatly decrease the production-related emissions. In this scenario, nitrogen is produced through an air separation unit, and nitrogen and hydrogen react in the Haber Bosch process to give ammonia. It is interesting to note that apart from its application in the fertilizers industry, low-carbon ammonia could be used to store and transport hydrogen and as a green fuel.

The main challenge in green ammonia production lies in the fluctuating nature of the renewable energy sources, leading to a variable hydrogen input in the process. To address this challenge, there are two main options: implementing large energy storage or operating the ammonia plant with a flexible load. The second option avoids large hydrogen storage, decreasing the associated safety risks and possibly reducing the ammonia cost.

This thesis aims to verify the operability of a load-flexible green ammonia plant. With this aim, the Haber Bosch process is dynamically simulated in UniSim Design R492. This simu-

1

lation is completed with the study of different control structures to maintain the pressure and temperature in the desired ranges.

2. Design and Simulation

In this section, the chosen design and the assumptions adopted when conducting the simulation in UniSim are reported. To understand the plant design it is useful to have a general introduction on ammonia production. The synthesis reaction is given in Equation 1. It is an equilibrium reaction, highly exothermic and that occurs with a decrease in the number of moles. Therefore, according to the Le Chatelier principle, it is favored by low temperatures and high pressures. However, excessively low temperatures hinder the reaction kinetic. The synthesis conditions are a compromise between kinetic and thermodynamic, resulting in a catalytic process conducted at temperatures between 350 and 550 °C and pressures between 150-200 atm. The catalyst used is an iron catalyst promoted with non-reducible oxides. Given that the single pass conversion is approximately 30%, the product is separated, and the unreacted gas is recycled.

$$3H_2 + N_2 \rightleftharpoons 2NH_3 \qquad (1)$$

With these bases, it is possible to understand the chosen plant layout. The makeup gas, hydrogen and nitrogen, is compressed to the synthesis pressure of 150 bar through a compression train and then mixed with the recycle flow. To circulate the gas in the synthesis loop, another compressor is used. The gas is sent to the converter, where it is partly converted into ammonia. Afterward, the gas mixture is cooled to about 0°C, allowing for the separation of the product from the unreacted gas, which is recycled. Looking more specifically at the reactor design, the one chosen for this project refers to the Topsoe S-300 converter. It comprises three catalytic beds with two intercoolers, where the cooling medium is the reactor feed. Part of the heat produced in the reaction is used in a waste heat boiler (WHB) and in the feed effluent heat exchanger (FEHE). The chosen ammonia production rate of the plant, at 100% load, is 10000kg/h.
To simulate the plant, the work is divided into two parts. First, a partial simulation, considering only the reactor, the feed effluent heat exchanger, and the waste heat boiler, is implemented. Second, the entire Haber Bosch process is simulated and the pressure control methods are studied. The partial simulation allows for an analysis of how a load decrease affects the reactor temperatures. Looking more specifically at the method used in the simulations, the catalytic beds are modeled as packed bed reactors in Unisim. The kinetic model used is the Nielsen model for ammonia synthesis. The kinetic parameters and the packed bed characteristics are estimated based on literature sources. Regarding the control structure, the option of implementing two controllers is considered: one on the waste heat boiler and one on the temperature at the inlet of the first catalytic bed. The process flow diagram of the partial simulation with the two controllers evaluated is shown in Figure 2. The results related to this partial simulation are summarized in Section 3.1.
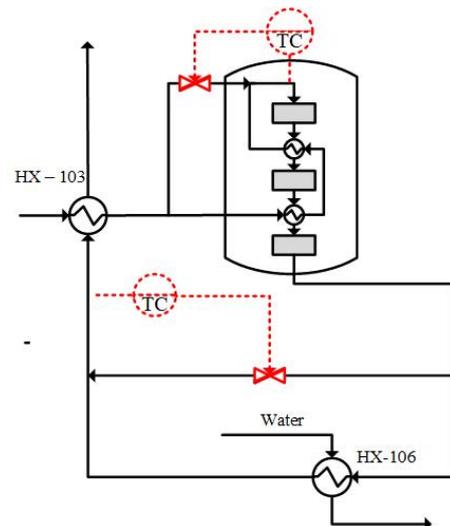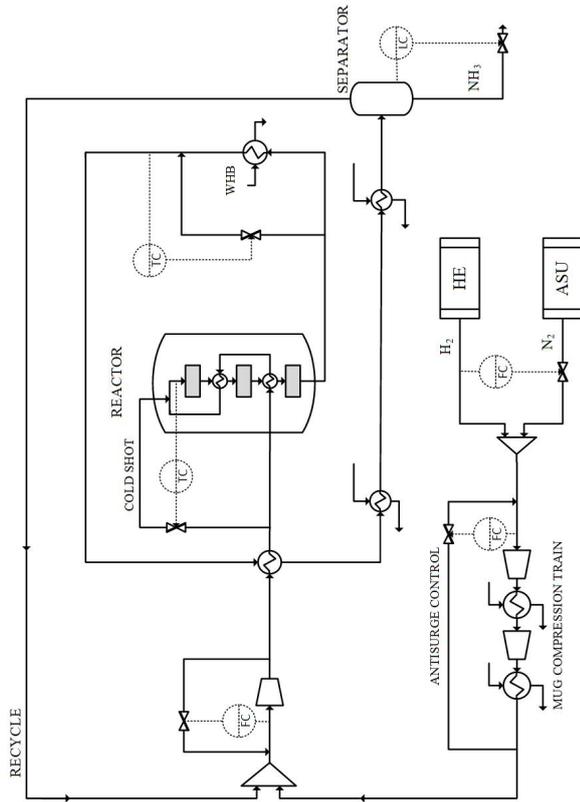

Figure 2: Process flow diagram implemented in the partial simulation, which includes the reactor with feed effluent heat exchanger and waste heat boiler, with two temperature controllers.
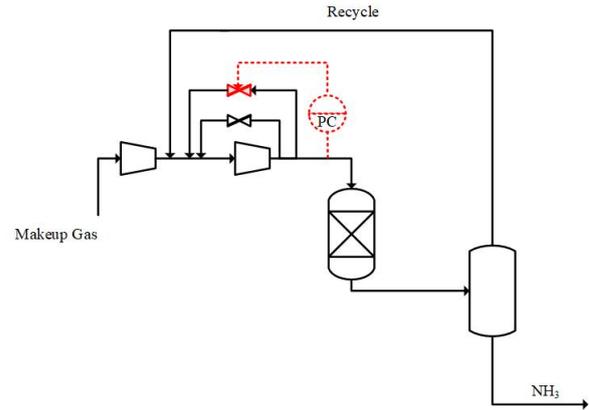
The second part consists of the study of the complete simulation, as reported in the process flow diagram in Figure 3. To describe how this simulation is conducted, more considerations are necessary. First of all, the load reduction in this case is achieved by decreasing the hydrogen flowrate, from 100 to 20% in three hours. To maintain the hydrogen-to-nitrogen ratio in the makeup gas, a flow controller is added to the nitrogen flow rate. The compressors are simulated by selecting the compressor rotating speed and implementing the compressor characteristic

curves from related literature. When the flow is reduced, the compressors could undergo surging, which needs to be avoided. Therefore, antisurge controllers are implemented both around the makeup gas compression train and around the recirculating compressor. Additionally, the level in the separator is controlled.
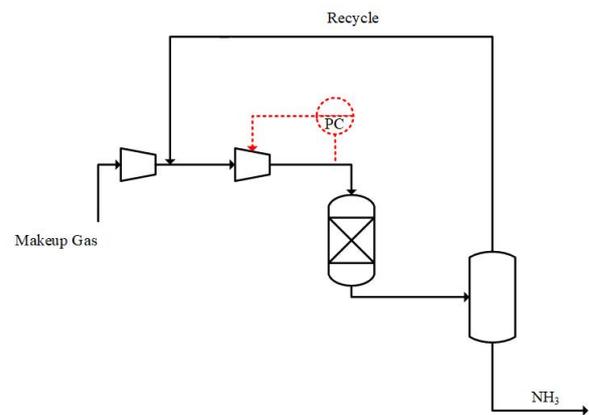

Figure 3: Process flow diagram implemented in the complete simulation, without any pressure control.

Conventional ammonia plants do not feature a pressure control method. However, in load flexible green ammonia plants, this may be necessary. For this reason, various pressure controllers are tested in the simulation. The first and most straightforward configuration would be to control the pressure by adjusting the recirculating compressor rotating speed, as shown in Figure 4. This however could be unfeasible in large plants, where the recirculating compressor and the makeup gas compressor are usually on the same driver.

Figure 5: Scheme of pressure control which uses a second loop around the compressor as manipulated variable. All the other controllers are omitted in the figure for clarity, even though they are in the simulation.

Figure 4: Scheme of pressure control which uses the compressor speed as manipulated variable. All the other controllers are omitted in the figure for clarity, even though they are in the simulation.

Another option is to use the antisurge line around the recirculating compressor as the manipulated variable for pressure control [2, 4]. If, for safety reasons, this valve should not be used, a second line parallel to the antisurge line can be implemented, as shown in Figure 5.

Other pressure control methods imply the introduction of a valve along the synthesis loop [2, 3], as reported in Figures 6 and 7.

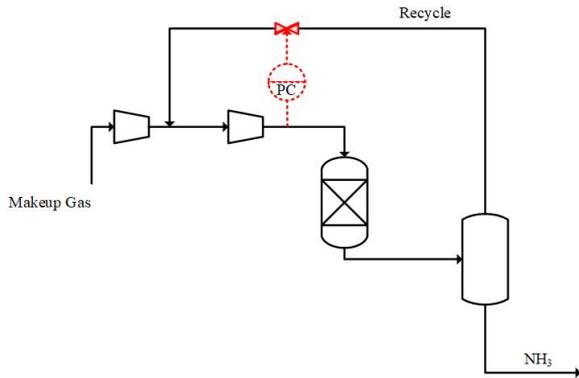All the controllers are tuned with the SIMC rule for PI (proportional, integral) controllers [5].

Figure 6: Scheme of pressure control which uses the recycle valve as manipulated variable. All the other controllers are omitted in the figure for clarity, even though they are in the simulation.
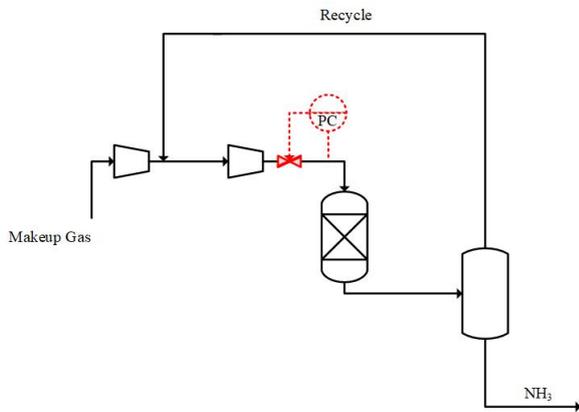

Figure 7: Scheme of pressure control which uses the valve after the compressor as manipulated variable. All the other controllers are omitted in the figure for clarity, even though they are in the simulation.

3. Main Results

When a load reduction is simulated with no temperature or pressure control, the pressure in the reactor decreases, which causes a decrease in conversion and therefore in the reactor temperature. This result underlines the need for a control structure that keeps the operating conditions in the desired range: if the pressure decrease continues, it could result in system shutdown. Moreover, continuous pressure fluctuations can impose a mechanical strain on the equipment decreasing its lifetime. In the next paragraphs, the dynamics of the system and possible control structures are analyzed.

3.1. Reactor and temperature control

In this section, the results of the partial simulation, comprising only the reactor, feed effluent heat exchanger, and waste heat boiler, are summarized. When the load is reduced without temperature control, the simulation shows that the temperature range in the reactor exceeds the catalyst operating range, primarily due to the waste boiler using more heat than is optimal. Therefore, a bypass stream is implemented around the waste boiler, and the flow is controlled to keep the temperature in the desired range. Despite this control, the temperature range in the reactor widens, with the lower temperature decreasing and the upper one increasing. This is most likely due to the heat exchangers that are more efficient than needed when the load is reduced. To maintain the desired operating range, a cold shot stream can be added, as seen in Figure 2. This consists of part of the reactor feed and it is sent directly to the first catalytic bed, bypassing the heat exchangers in the reactor. The flow rate of this stream, called cold shot, is adjusted to control the inlet temperature to the first catalytic bed. The outcome of having these two temperature controllers in the reactor can be observed in Figure 8, which reports the temperatures at the inlet and outlet of each catalytic bed during a three-hours reduction of flow rate from 100 to 20%.
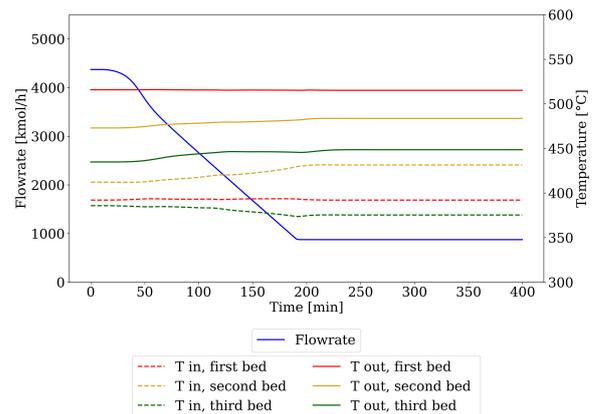

Figure 8: Partial simulation, temperatures in the reactor when the flow at the reactor inlet is reduced from 100% to 20 % in three hours, and two temperature controls are implemented.

As it is possible to observe, the temperature range is practically maintained.

3.2. Complete System and Pressure Control

This section summarizes the results obtained from the complete simulation when the load is reduced and different pressure control methods are considered. In all the reported results, the hydrogen flow rate is decreased from 100 to 20% in three hours. If the conversion in the system remains relatively stable, the hydrogen decrease causes the flow rate in the loop to decrease accordingly. Regarding the pressure, the considerations differ based on the control method chosen.

3.2.1 The use of the compressor speed for pressure control

Using the recirculating compressor speed as a pressure control proves to be very effective in this simulation, as it is possible to observe in Figure 9. When the pressure decreases, the rotating speed decreases to keep the gas in the loop. The results show a speed decrease from 6400 to 945 rotations per minute. The main drawback related to this method is that the recirculating compressor and makeup gas train are usually on the same driver. Therefore, the recirculating compressor speed may not be a degree of freedom that can be selected as the manipulated variable.
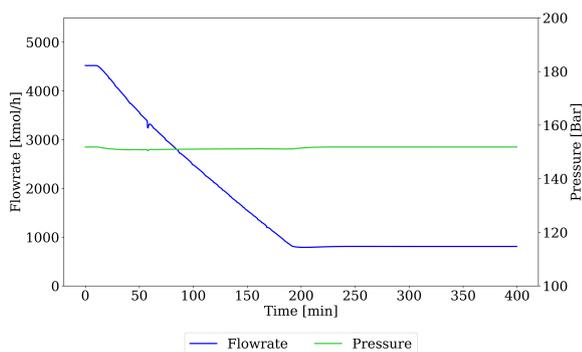
Figure 9: Flow and pressure at reactor inlet resulted from a hydrogen load decrease from 100% to 20% in 180 minutes, using the recirculating compressor speed as the manipulated variable for pressure control.

3.2.2 The use of a second antisurge line for pressure control

Some of the main results of using the second antisurge line as the manipulated variable for pressure control are reported in Figure 10. When the

load is decreased and the pressure decreases, the valve opens in the attempt to keep constant the amount of gas in the loop and, consequently, the pressure. This method results to be less effective than the previous one, but it does not require changing the compressor speed.
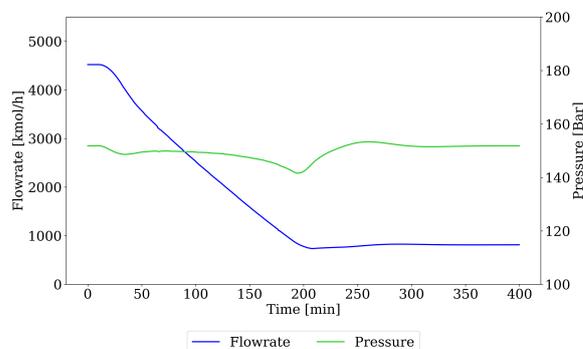
Figure 10: Flow and pressure at reactor inlet resulted from a hydrogen load decrease from 100 % to 20% in 180 minutes, using an additional line around the compressor as the manipulated variable for pressure control.

3.2.3 The use of a valve in the loop for pressure control

In Figure 11 the results related to using a valve in the recycle stream are reported, while in Figure 12 the valve is positioned after the recirculating compressor. In both cases, when the flow is decreased, the valve closes, which retains the gas in the reactor, increasing the pressure.
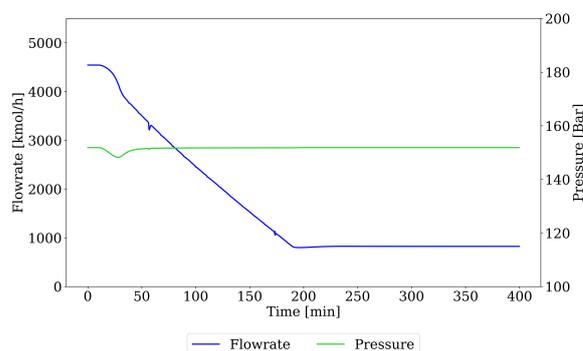
Figure 11: Flow and pressure at reactor inlet resulted from a hydrogen load decrease from 100 % to 20% in 180 minutes, using a valve in the recycle stream as manipulated variable for pressure control.
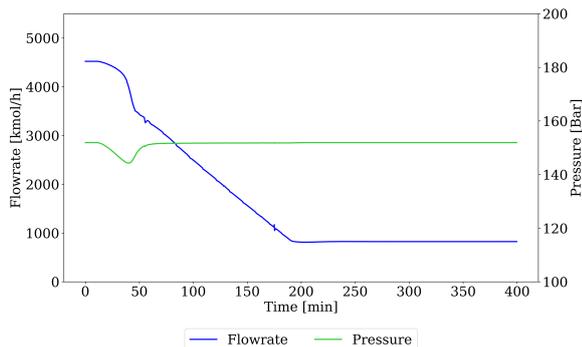
Figure 12: Flow and pressure at reactor inlet resulted from a hydrogen load decrease from 100 % to 20% in 180 minutes, using a valve after the compressor as the manipulated variable for pressure control.

These two methods give quite similar results, in between the two previously analyzed, therefore the addition of a valve in the loop could be particularly interesting in the case of frequent load changes.

3.3.   Effect of the Separation Temperature

When the load is decreased and the separation temperature is not controlled, the latter decreases, as the coolers are sized for 100% load. A lower separation temperature results in a more efficient separation, leading to a lower percentage of ammonia in the recycle stream and, consequently, at the reactor inlet. A lower ammonia concentration in the reactor feed favors the thermodynamics of the process, leading to higher conversion and temperature in the first catalytic bed. This is particularly interesting in the case of a continued low-load operation when catalyst overheating can occur. Since the highest temperature in the reactor is reached in the first catalytic bed, the overheating of the catalyst may be mitigated by increasing the separation temperature.

4.   Conclusions

In conclusion, this work suggests that it is possible to operate a load-flexible green ammonia plant. The partial simulation, considering only the reactor, feed effluent heat exchanger, and waste heat boiler, indicates that the temperature range can be maintained with the implementation of two temperature controllers. When considering the complete simulation and the

pressure control, the most effective pressure control method results in the use of the recirculating compressor speed as the manipulated variable. When this is not possible for economic reasons, the implementation of a valve in the loop emerges as an efficient alternative. Further work may include more detailed modeling that considers all the space directions in the reactor and includes compressor characteristic curves specific to the studied plant. Additionally, it would be interesting to integrate this simulation with a simulation of the water electrolysis, in other to optimize the respective plant design, and to design the eventual energy storage required. The work may then be concluded with an economic analysis.

5.   Acknowledgements

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