Ammonia Plant : Modelling on VALI 5

Ing. A. HOUBEN
Ing. N. MONFORT
Ir C. CHARLIER
HELMo Gramme – Liège
Belsim Engineering

Le présent travail propose une modélisation du procédé de fabrication d'ammoniac (Haber-Bosch) sur le logiciel VALI de la société Belsim Engineering. Ce modèle a permis de réaliser une étude en simulation du comportement du procédé, en fonction de certains paramètres clés et de mettre en valeurs les résultats. Une étude commerciale a également été menée afin d'étendre le marché actuel de la société.

Mots-clefs : Unité Ammoniac – Data Validation & Reconciliation – Simulation – Modélisation – Gestion de procédé.

The present work gives a modelling of ammonia manufacturing process (Haber-Bosch) on VALI software from Belsim Engineering company. This model allowed to realise a simulation study of the process, in terms of key parameters and to highlight the results. A commercial study has also been led in order to expand Belsim's current market.

Key words: Ammonia Plant – Data Validation & Reconciliation – Simulation – Modelling – Process management

1. Introduction

Nowadays, the control development of chemical processes is increasingly important considering economic, political or environmental issues are related, making them even more dependent on this control.

The collection of process data allows relevant and reliable performance variables to be calculated provided that the data are correct. Indeed, all these data must be consistent with several constraints, among others such as mass, energy or pressure balances.

Belsim Engineering looks for opportunities to extend its activities in new sectors. Indeed, their core business is to provide Data Validation & Reconciliation (DVR) solutions at present mainly in Oil & Gas industry and power generation area.
Therefore, the company wants to investigate other chemical processes, such as ammonia manufacturing being among the most important productions.

The objective of the work was therefore to model a unit of ammonia manufacturing on the new version of VALI to get use of new tools in order to highlight influence parameters of the process. A data collection was led at Yara, an ammonia producer whose one of their ammonia plant is located in Belgium, allowing to compare model results with their values.

In general processes, the strenghthening of process control is more and more essential and becomes a challenge for process mastery.

In order to control a process, Key Performance Indicators (KPI's) are calculated and allow to point out the process health. In order to perform this, coherent and trustable data are needed and they must respect different constraints such as mass, energy and pressure balances for example and as the first main ones. Belsim has already understood the challenge surrounding process controls by providing DVR solutions to its current customers.

VALI Software, whose last update is VALI 5, allows to calculate these KPI's and helps process engineers to improve their own process knowledge and control.

With this in mind, a simulation modelling of ammonia manufacturing has to be implemented in VALI 5. The knowledge of Yara's ammonia process is very useful to create such a model as close as possible from a real one. Finally, this model has been used in order to check if it behaves like or close to the real process and influencing parameters have to be highlighted to create the final Vali Processing leaflet.

2. Data Validation & Reconciliation

2.1. DVR definition

Data Validation & Reconciliation is a powerful tool based on statistical principles which allows to control the health of a process by performing numerical calculations with the measurements, allowing to reduce their uncertainties and/or to point out a measurement incoherence.

2.2. Splitter example

To understand how DVR works, a good example is the case of mass balance management on a splitter. A feed stream a is divided into outlet streams b and c thanks to the splitter equipment shown in Figure 1. According to chemical engineering theory, a mass balance equation links the different streams.

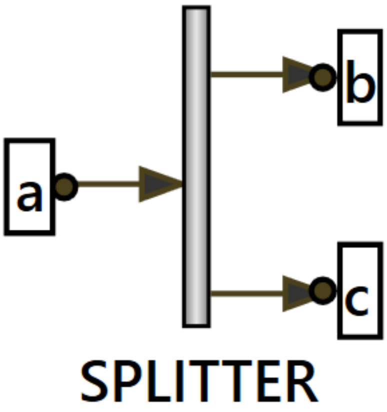

Figure 1 : Splitter Example

Four statements can be established by this model:

- Global mass balance is given by $a = b + c$
- Composition of the three streams are identical.
- As all compositions are identical, this leads to one mass balance.
- The mass flow rates of a, b and c are different.

So, there are:

- **3 variables:** a, b and c.
- **1 equation:** $a = b + c$

Degree of freedom (D.O.F) is defined as the minimum number of information needed to be able to calculate the system. In other words, degree of freedom is given by the difference between number of variables and number of equations available. In this case, D.O.F is given by:

$$\begin{aligned} \text{D.O.F} &= \#\text{Variables} - \#\text{Equations} \\ &= 3 - 1 = 2 \end{aligned}$$

Two measurements are necessary to lead to 1 unique solution. However, it is impossible to know if it is the right solution, or not. And that is why DVR is therefore more interesting and reliable. Indeed, if three flow rate measurements are available on the streams a, b and c, DVR can reconcile these values and improve the knowledge of the process.

2.3. Redundancy

In a same aspect, redundancy (Red) of this system can be defined as follows:

$$\text{Red} = \#\text{Measurements} + \#\text{Equations} - \#\text{Variables}$$

According to its definition, three cases can be considered:

- **Red = 0:** the system is completely defined. There is a unique solution. In process modelling, this case is called **Simulation** which means that the number of data inserted to the model is just enough to calculate all the others. The problem occurs when some data are not correct and not well measured.

- **Red > 0:** the number of measurements is higher than needed. There are too many constraints. According to a simple analysis, such an alternative cannot be solved but with DVR, VALI is able to handle it. Additional measurements allow the user to criticize all the others, that is why uncertainties are determinant.

- **Red < 0:** there is not enough measurement to solve the system. There are infinite solutions.

2.4. Objective function

In a way to satisfy all the constraints such as mass and energy balances for example, objective function consists in minimizing the sum of all the penalties of the model. This function is defined as follows:

$$\text{Objective function} = \text{Min}\sum_i \left(\frac{y_i - y_i^*}{\sigma(y_i)}\right)^2 = \text{Min}\sum_i Penalty_i$$

Where:

- y_i is the **measured** value.
- y_i^* is the **reconciled** value (after DVR calculation).
- $\sigma(y_i)$ is the **standard deviation** on the measurement y_i.

When the user gives a **measurement** as data, this one should be right, i.e. it represents perfectly the real measurement. However, we are not sure this measurement is correct. That’s why they are accompanied by a **standard deviation** which leads to a range around the given value which is considered acceptable. If some coherences are detected, the measurement has to be **reconciled** and therefore it is translated by its **penalty**.

3. Ammonia Plant

3.1. Generalities

General properties

Ammonia is the reference for nitrogen uses and is a basic tendency substance that is neither very reactive nor highly flammable. Ammonia has a very important role in the nature because it contains nitrogen which is involved, in its combined and reactive forms, in all metabolic processes. Ammonia is well known for its strong smell which allows to detect it from 20 ppm and starts to be dangerous from 1000 ppm in air. It is an achromatic and volatile compound as well as it is soluble in water forming NH_4OH until around 35% in weight.

Economic aspects

Since ammonia is a reference product, worldwide production is increasing more and more through the years. Since 1985, it has been the first synthetic industrial product to exceed a worldwide production of 100 MT.

According to the latest report (USGS, 2018), worldwide production of ammonia was 144 MT in 2016 and reached 150 MT in 2017.

Ammonia uses

More than 75% of ammonia is used for fertilizer industries while the remaining 25% are used for finest chemistry such as dyes, fibers, pharmaceuticals, insecticides, cleaning products, … Common fertilizers are urea, ammonium nitrate, ammonium sulphate and ammonium phosphate.

3.2. Haber-Bosch Process

Ammonia production is an integrated process where all the parts are linked and influence each other. The process can be divided [1] between five different parts:

1. Reforming (primary and secondary)
2. Shift Conversion
3. CO_2 Removal
4. Methanation
5. NH_3 Synthesis

Figure 2 gives a simplified view of the process where ammonia production is shown at the last part of the simplified flowsheet presented. Global structure of VALI simulation model is going to follow as much as possible this operational scheme.

It is an integrated process which means that the first step is to create synthesis reagents. This is the **reagents preparation (primary and secondary reforming)**. Indeed, ammonia production is based on the simple reaction:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad \Delta H_R = -46.1\ kJ/mol$$

Where N_2 comes from atmospheric air while H_2 has to be produced.
Before that, some impurities or non desirable compounds such as CO and CO_2 (byproducts) have to be removed by different ways because they are poison for NH_3 synthesis catalysts.

This is the **reagents purification (Shift Conversion, CO_2 Removal and Methanation)**. Finally, when all the impurities have been removed from the mixture, ammonia synthesis can take place. This is the **end product synthesis (NH_3 Synthesis)**. This mixture can be purified in order to have a pure ammonia production.

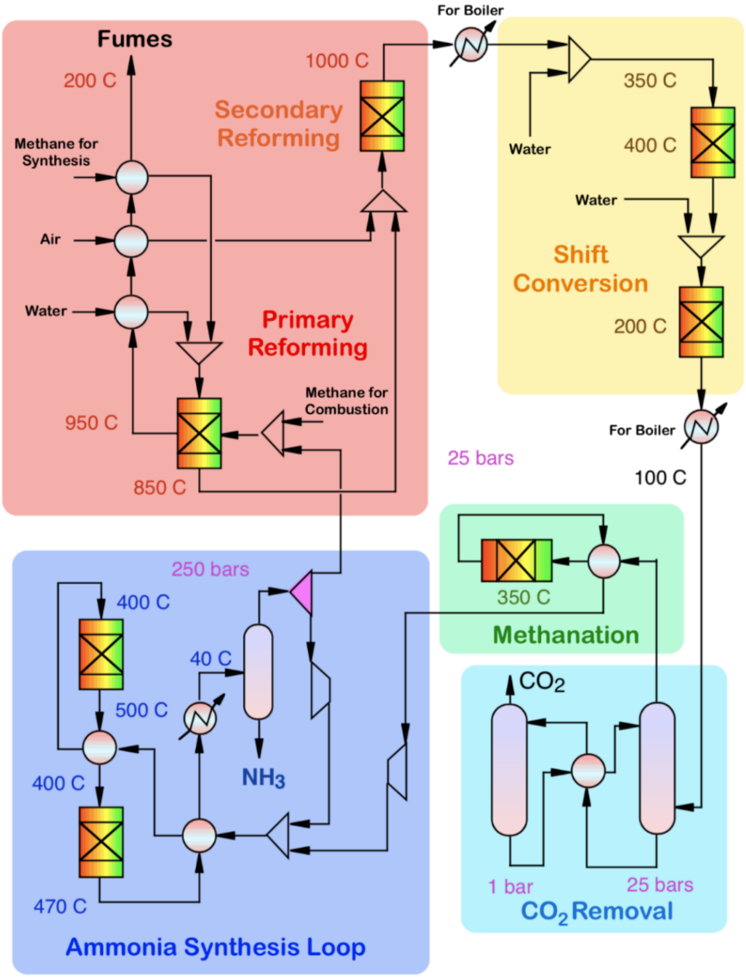

Figure 2 - Ammonia Manufacturing Flowsheet (Haber-Bosch)

4. Study of Operationnal Paramaters

On the reforming side, most of the involved reactions are pressure sensitive. Indeed, inlet pressure is an interesting parameter to follow, as it has a direct impact on reformer efficiencies. Therefore, a first analysis on natural gas[1] consumption vs inlet pressure is worth pursuing.

This first analysis is made with the following assumptions (whatever the inlet pressure):

- Ammonia production is fixed at 1086 tons per day.
- Ammonia synthesis pressure level is fixed at 136.7 barg.

As shown in Figure 3, natural gas consumption decreases as the inlet pressure increases. However, regarding **steam methane reforming reactions**, the higher the pressure, the lower the hydrogen yield according to reaction 6.1.1. Therefore, for a same ammonia production, the amount of natural gas should be lower since methane conversion is better at lower pressure.

Actually, even if the methane conversion is lower when working at higher pressure levels, the global consumption of natural gas is anyway higher because more energy must be brought in for the synthesis gas (CO and H_2 mixture) compression. Indeed, global natural gas comsumption is also linked to the mechanical energy needed by the whole process. Working at higher pressure allows to reduce the energy needed by the compressors to reach the same pressure level at synthesis side.

Steam methane reforming reactions are given as follows:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \tag{6.1.1}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{6.1.2}$$

It appears there is a **minimum natural gas consumption** around 41 barg. Indeed, this model has been designed according to Yara's data. These chosen values seem to reach a minimum value for natural gas consumption as the curve shows.

For higher pressures greater than 43 barg, it can be shown that natural gas consumption now increases. However, such pressure levels are not relevant in a real process as natural gas is supplied at around 45 barg. Therefore, the model should integrate a compression stage to reach a higher pressure level at reforming than the

---

[1] Natural gas is a gas mixture of hydrocarbons consisting primarily of methane (more than 90 %vol of CH_4), but also includes heavier alkanes and other compounds such as N_2, H_2S, CO_2, … In figure 2, methane for synthesis is mentionned in order to show that mainly CH_4 is involved in reforming reactions. In a real process, natural gas is used of course.

supplied one. This is probably not such a good idea because compression is expensive. Then, the model would not reflect real world operations.

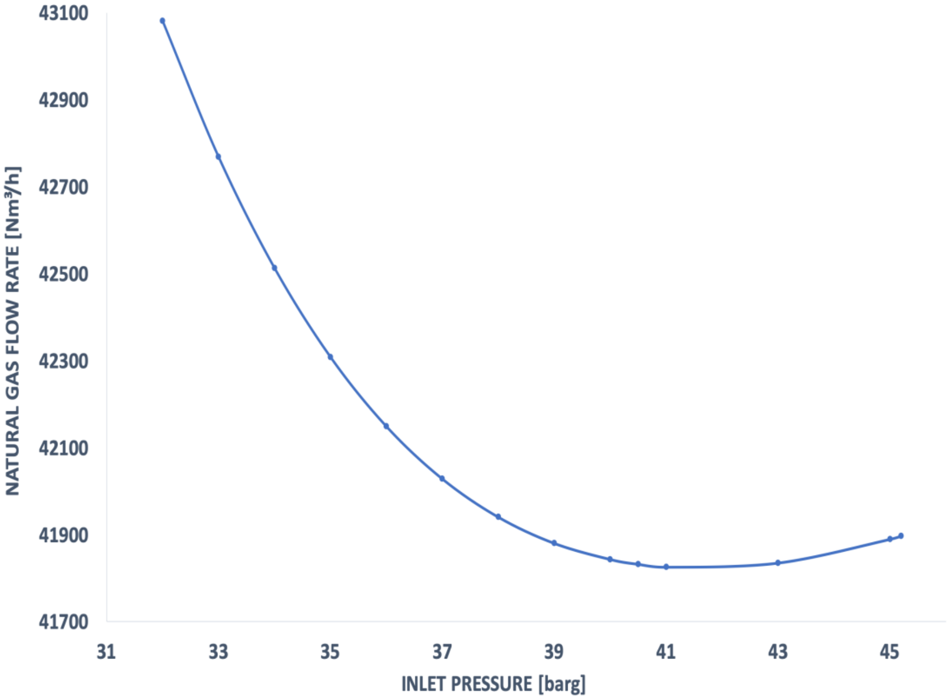

Figure 3 : Natural Gas Flow Rate vs. Inlet Pressure

In other words, the best way to reduce natural gas flow rate (i.e. its consumption) is to stay close to the supplied pressure of the natural gas sent by Yara's plant (around 45 barg). Indeed, it is more interesting to keep the supplied pressure of natural gas as the **compression work has already been delivered** by the natural gas supplier, such as Fluxys[2]. Therefore, there is no need to expand it even if the methane conversion would be better at lower pressure according to *Le Chatelier*'s principle.

---

[2] Currently, Yara is supplied by Fluxys for natural gas uses.

As shown in Figure 4, methane conversion at primary and secondary reforming decreases as inlet pressure increases. It is coherent thanks to *Le Chatelier*'s principle applied to steam methane reforming reactions. Indeed, reaction 6.1.1 is pressure sensitive as there is an increase of gas moles while reaction 6.1.2 is not pressure sensitive. However, pressure does not decrease the methane conversion too much, especially at secondary reforming where the pressure influence is almost negligible.

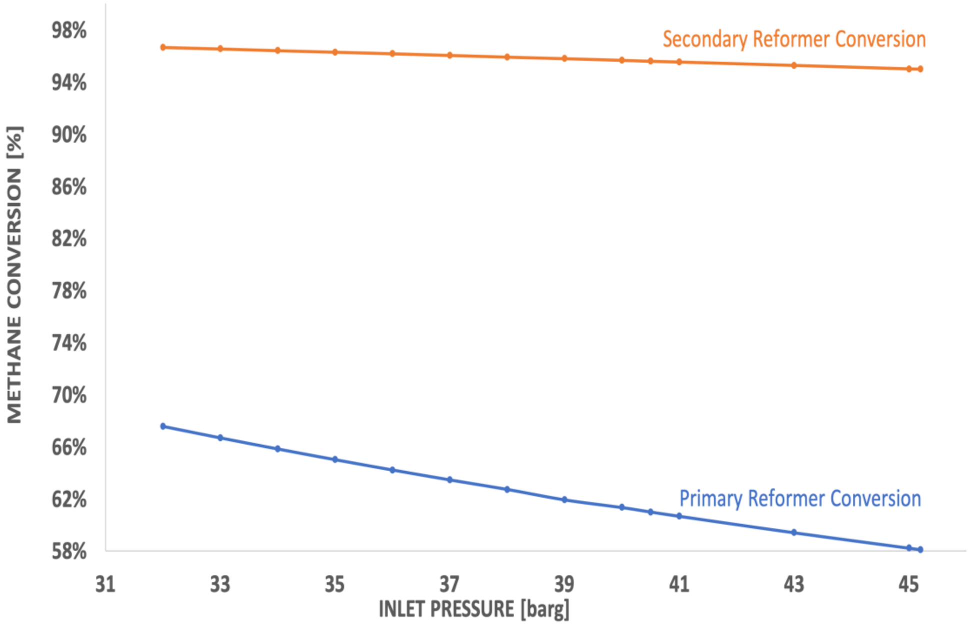

Figure 4 - Methane Conversion at Reformers vs. Inlet Pressure

To understand how natural gas consumption decreases with inlet pressure even if yields are lower, Figure 5 gives the different compression duties at air and synthesis gas compressors.

If pressure increases:

- The pressure level for the air compressor is higher, so the power required is higher.
- The pressure increase for the syngas compressor is lower, so the power required is lower.

However, the sum of these powers **decreases** when inlet pressure increases. Then, it is obviously more efficient to work at a closer pressure than the supplied one.

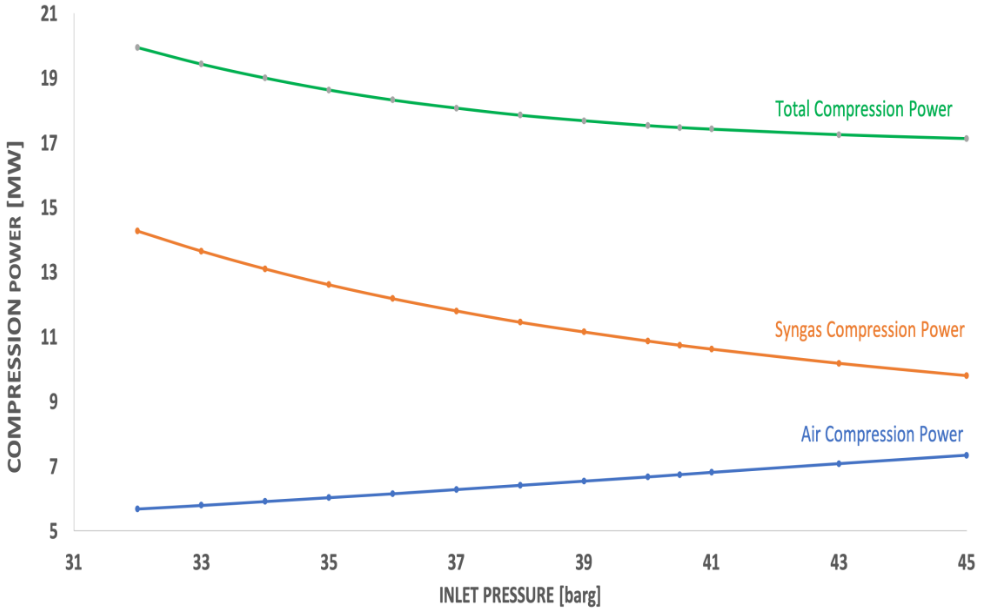

Figure 5 - Compression Power Duties vs. Inlet Pressure

Therefore, this analysis can explain why natural gas consumption decreases according to the pressure increase.

5. Conclusion

First of all, the modelling of an ammonia plant on VALI 5 is a good way to improve and deepen the knowledge and behaviour of the process. Indeed, ammonia process is diversified in terms of reactions, physical separations and heat management. It allows the use of the majority of standard equipments and understanding of how to insert them in an integrated process. This hard work can also be considered as a good approach and training on VALI 5.

Concerning the present work itself, the main task of modelling and understanding an ammonia process can be considered achieved as a fully functionnal model of ammonia manufacturing has been completely realised. Its behaviour is close to a real process, according to the precious data that have been collected at Yara. It has been demonstrated by the model that the optimum pressure which has been found is the same pressure operating in Yara’s process.

As it has been shown before, our model pointed out the influence of pressure at the reforming side.

Moreover, the model behaviour can be easily controlled as it is adequately configured: influencial parameters can be followed by monitoring only one parameter, for example the inlet pressure of natural gas.

As requested by Belsim, this strong modelling basis could be used as a demonstration model for potential customers where VALI benefits could be highlighted inside the model. Moreover, it is easy to add additionnal units and/or streams, as the main parts are already designed and configured.

Finally, the current model could be a strong basis for a real DVR application where a current ammonia process, for example Yara plant, could be modelled with this modelling basis. Then, real data from process measurements could be implemented on this specific modelling in order to perform DVR calculations and to improve the control of the process.

6. Sources

[1] CHARLIER, C. (2018). Chimie industrielle. *Deuxième partie - La chimie industrielle minérale*. Angleur, Liège, Belgique: HELMo Gramme.

[2] USGS. (2018, January). *National Minerals Information Center.* Retrieved from USGS: science for a changing world: https://www.usgs.gov/centers/nmic/nitrogen-statistics-and-information