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Multi-objective Optimization of Industrial Ammonia Synthesis

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Abstract

Ammonia is widely used in different applications - as an intermediate product in production of agricultural fertilizers, inorganic salts and explosives, or used directly as a solvent or refrigerant. The broad domain of applications, especially its importance for agriculture, puts ammonia synthesis in the basis of chemical industry. However, the process is mature and well developed, the improvements to be made towards it are still significant due to growing demand.

The use of mathematical models in chemical engineering has been extensively applied towards optimization of industrial process and proven itself to be an efficient technique. If done properly, it allows for finding best process conditions avoiding timely and costly experiments.

The objective of this thesis work is to perform optimization study of industrial ammonia synthesis and discover operational and/or design modifications to be done in order to improve performance of the process. Two parts of industrial ammonia synthesis have been considered - the converter carbon dioxide removal from process gas.

Firstly, the mathematical model for simulation of the industrial converter was developed. In order to fit main model parameters, the large array of industrial data was studied by means of cluster analysis. It allowed to extract the smaller subset of data to perform model fitting followed by validation. The simulations showed a good consistency between model and observed instrumentation reading from the ammonia plant. Further, few case studies were performed in order to find optimal set of process parameters allowing for improved performance. The main controlling parameters are temperature of feed, converter pressure, ratio of quenching stream to primary feed and catalyst distribution of among beds.

Secondly, an optimization of carbon dioxide removal stage from process gas was performed. The aim was to improve solvent recovery and boost carbon dioxide liberation. Ranking of major process controlling parameters was performed with random forest algorithm and Boruta. It allowed to narrow down the number of model parameters from more than 10 to 4. Further optimization search allowed for finding the best combination of these parameters to achieve better solvent regeneration.

Keywords: Ammonia synthesis, Modelling, Multi-objective optimization

Co-Authorship statement

The work presented in the current thesis is collaboratively done by the author, Dr. Ajay Kumar Ray and plant engineers from the company the author and Dr. Ray worked with - Scott Link, Brian Bloxam and Bratin Ghosh. The personal contribution described below applies to the content of every chapter presented in the thesis.

The author did a literature review and study of a theoretical background, research methods and performed data retrieval from the plant. Also, the author developed all modelling work - incorporated the model equations found in literature, derived missing equations and developed a code to solve them. Additionally, the author performed simulation and interpretation of obtained optimization results. All chapters are solely written by the author.

Dr. Ajay Kumar Ray did a supervision of the entire thesis work, consulted on every step of model development and its applicability towards the existing plant. Also, he advised on results interpretation and their delivery to the plant engineers.

Material on the optimization methods in chemical engineering was partly published as book chapter in *Catalytic reactor* ed. by Basu Saha (2016). Chapters 2,3 will be submitted a single paper entitled “Modelling and multi-objective optimization of industrial ammonia converter”. Chapter 5 will be published as “Multi-objective optimization of industrial ammonia converter under catalyst deactivation”.

"...where was no one who knew for certain what happiness is and what exactly is the meaning of life. And they had accepted as a working hypothesis that happiness lies in the constant cognition of the unknown, which is also the meaning of life."

"Monday Begins on Saturday", Arkady and Boris Strugatsky

Acknowlegements

Dedicated to my entire family, in its widest sense possible.

To my lovely wife:
Without your support and patience I would not be able to make it.

To my grandfather:
You always believed in me and made me who I am now. You have started this journey with me but did not see how it's ended. You are always in my heart. I love you, grandpa!

To my grandmother:
Thanks for being fun and supportive, for long-lasting discussions and your endless wisdom.

To my mom:
I am endlessly grateful for your patience, love and for permanently covering my back!

To my dad:
Appreciate your advice even when I disagree with you.

To my other mom and dad:
I have been honoured to be the part your family all these years. I hope you are not disappointed with me and will never be.

To my friends:
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To Scott Link, Brian Bloxam and Bratin Ghosh:
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Contents

List of Figures

List of Tables

Chapter 1

Introduction

Nomenclature

DM	decision maker
g	inequality constraint
G	goal in goal programming method
GA	genetic algorithm
h	equality constraint
I	objective function
J	number of equality constraints
K	number of inequality constraints
l_{str}	length of binary string
MOO	multi-objective optimization
n	number of objectives
R	penalty parameter
S	decision domain
SA	simulated annealing
SGA	simple genetic algorithm
SOO	single-objective optimization
x	decision vector

Greek letters

δ	deviation
ϵ_i	constraint
Ω	penalty term

1.1 Preface

Ammonia is one of major chemicals produced in the industry. It has a variety of applications: for manufacturing of inorganic salts, polymer fibers, explosives, etc. (Fig. 1.1) Especially, it is essential chemical in production of agricultural fertilizers: as an intermediate in urea synthesis or used directly as liquid. It is hard to diminish the importance of ammonia for agricultural sector all over the world, and in North America in particular.

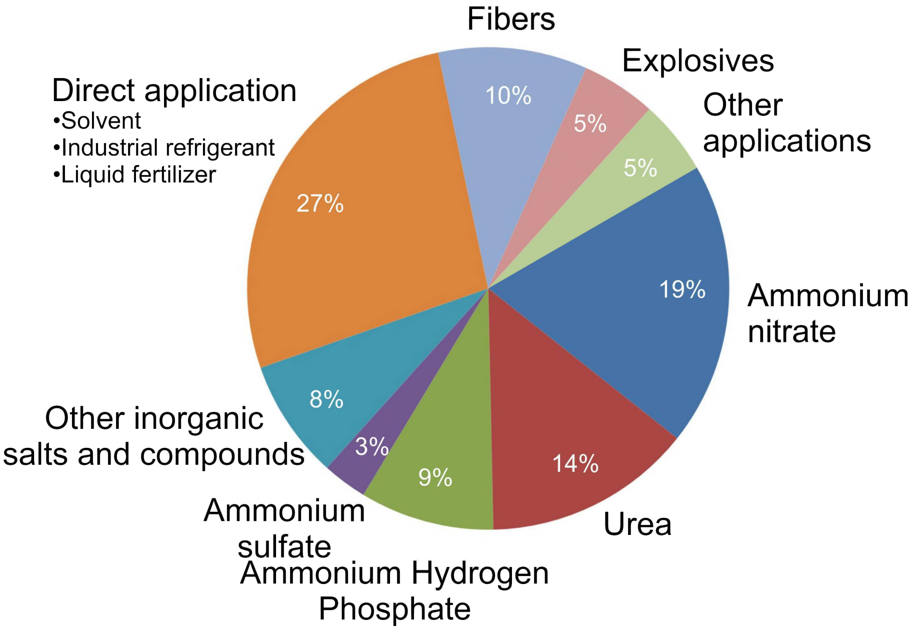


Figure 1.1: Applications of ammonia[1]

Ammonia is produced all over the world. Largest gross producers are Asian countries and former Soviet Union. Middle East and North America are not far behind. However, not all the regions are self-sustainable supply-wise. North America, even having a large production, is still net importer of ammonia.

Moreover, ammonia market is continuously growing. Total world ammonia demand has been steadily increasing over last decade at rate of 2.2 % per annum.[2] In order to satisfy for the demand of an already deficit market it is imperative to go both ways simultaneously - build new facilities as well as intensify production at existing ones.

We put planning, design and development of new production facilities outside of the scope of this work, while focusing on enhancements in ammonia synthesis. As with any chemical engineering process, there is a vast number of ways to improve performance of an industrial process. Regardless of the objectives for improvement, this may be done through, among others, physical modelling, data analysis and data-based modelling, first-principle mathematical modelling and numerical optimization.

One can not neglect the power of process modelling and numerical optimization for chemical engineering processes. Developing robust models allows for accurate process simulation. Therefore, one can perform a comprehensive study of a process without expensive physical modelling and/or use the model for the numerical optimization to boost up process performance.

Moreover, since major chemical engineering plants introduced digital process control for continuous operation a large amount of data has become available. It is wise to take advantage of the fact to assist for development of more accurate and relevant models or improve existing ones.

1.2 Overview of Industrial Ammonia Synthesis

1.2.1 Ammonia properties and synthesis reaction

Ammonia is a chemical compound formed by one nitrogen and three hydrogen atoms. Geometrically, ammonia molecule is a tetrahedron with atoms in its apices (Fig. 1.2).

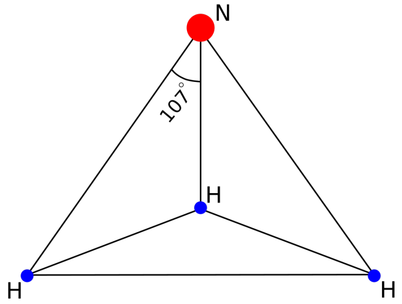


Figure 1.2: Ammonia molecule configuration

Table 1.1: Equilibrium fraction (% mol.) of ammonia in stoichiometric mixture H_2:N_2

t, °C	P_{abs}, MPa			
	5	10	20	30
300	39.38	52.79	66.43	74.20
350	25.12	37.60	52.17	61.31
400	15.23	25.15	38.53	47.86
450	9.12	16.23	27.15	35.57
500	5.56	10.39	18.61	25.54

The angle between nitrogen and hydrogen atoms is 107 °. This along with nitrogen's electronegativity makes molecule highly polarized with dipole moment 1.5D. In many aspects ammonia behaves similarly to water in chemical reactions, both are diamagnetic and able to dissolve many materials.[1]

At standard conditions (15 °C and 101.3kPa) ammonia is transparent gas with pungent odor. It is a highly volatile chemical compound with vapour pressure 728.3 kPa at standard temperature. Ammonia is synthesized through the following reaction:

$$N_2 + 3\,H_2 \longleftrightarrow 2\,NH_3, \quad \Delta H^0_{298} = 46.22 \quad \text{kJ/mol} \tag{1.1}$$

The reaction 1.1 is limited by equilibrium, therefore does not go all the way to the product. Ammonia synthesis reaction equilibrium has been extensively studied and data on equilibrium is available for use.[1,3] As one can see from Table1.1, lower temperatures and higher pressures are much in favour of ammonia equilibrium.

However, the reaction is kinetically slow. Therefore, elevated temperatures are necessary to provide significant yield and make synthesis process somehow efficient. So equilibrium-wise, Eq.1.1 is carried out in such conditions that compromise between high thermodynamic equilibrium ammonia concentration and fast reaction rate. Also, the reaction's exothermicity plays a role as liberated heat slows it down at any process conditions.

Even though, the reaction is exothermic and supposed to react spontaneously, it does not happening due to high energy input required to overcome activation barrier. One of major reason is that nitrogen as a molecule is highly inert and does not easily involved into chemical interactions. Energy of its dissociation is around 941 kJ/mol. The activation energy itself for homogeneous reaction of nitrogen and hydrogen is reported in the range 230-420 kJ/mol. In order to overcome this barrier the temperatures of 650-1000 °C are necessary.[1] However at this conditions, yield of ammonia is low due to reaction equilibrium. Therefore, in order to make process feasible at reasonable industrial condition the presence of catalyst is necessary to reduce energy barrier of reaction[4].

Activation energy of ammonia synthesis over heterogeneous catalysts is fairly lower - around 100-160 kJ/mol. This drastically reduces reaction temperature down to 250-400 °C. Historically, the synthesis catalysts used for industrial scale production have predominantly been iron-based with promoters from non-reducible oxides (*i.e.* CaO,Al_2O_3,MgO,SiO_2). Iron is used in forms of Fe(II)-Fe(III) oxides mixtures in about even ratio. Later generations of catalysts have been based on ruthenium as an active metal. Ru-based catalysts appeared to be more active and able to reduce process temperature and pressure even further. However, majority of ammonia plants nowadays are still utilizing Fe-based catalysts.

Ammonia synthesis is a mature process and extends back over decades, but theres still no consensus about reaction mechanism on the surface of catalyst. There have been many studies conducted to investigate mechanism of reaction 1.1 on heterogeneous solid catalyst.[5] According to the most common theory found in literature, it is a surface based-reaction where nitrogen dissociation is considered as a rate-limiting step. Hydrogen and nitrogen molecules are both adsorbed on catalyst surface and then dissociate to atomic state. It can be summarized as a number of following steps[1]:

$$\begin{aligned}
&\mathrm{H_2} + * \rightleftarrows 2\mathrm{H_{adsorbed}}\\
&\mathrm{N_2} + * \rightleftarrows \mathrm{N_{2,adsorbed}}\\
&\mathrm{N_{2,adsorbed}} \rightleftarrows 2\mathrm{N_{adsorbed}}\\
&\mathrm{N_{adsorbed}} + \mathrm{H_{adsorbed}} \rightleftarrows \mathrm{NH_{adsorbed}}\\
&\mathrm{NH_{adsorbed}} + \mathrm{H_{adsorbed}} \rightleftarrows \mathrm{NH_{2,adsorbed}}\\
&\mathrm{NH_{2,adsorbed}} + \mathrm{H_{adsorbed}} \rightleftarrows \mathrm{NH_{3,adsorbed}}\\
&\mathrm{NH_{3,adsorbed}} \rightleftarrows \mathrm{NH_3} + *
\end{aligned} \tag{1.2}$$

A number of kinetic rate expressions were proposed in the literature to describe synthesis reaction.[6–10] The Temkin equation (Eq.1.3) is found to be most accurate and applicable, therefore used for the model. The equation is able to reflect equilibrium limitations as well as the reaction's mechanism.

$$R_{NH_3} = k_2 \left[K_a^2 f_{N_2} \left(\frac{f_{H2}^3}{f_{NH_3}^2} \right)^{\alpha} - \left(\frac{f_{NH_3}^2}{f_{H_2}^3} \right)^{1-\alpha} \right] \tag{1.3}$$

1.2.2 Ammonia synthesis technology

Within industrially feasible operation range, production of ammonia is limited by unfavourable equilibrium of the reaction, so only around 15-30 % mol. NH_3 is possible to obtain per converter pass. Therefore, use of recycle stream is necessary to separate ammonia from unconverted gas. Then the stream is combined with a make up and returned to a converter. Secondly, due to presence of inerts with a loop (mostly CH_4 and Ar), part of recycled stream is withdrawn to purge stream. Moreover, due to large amount of generated heat, synthesis loop is equipped with heat recovery system. However, the actual loop arrangements varies for different technologies and depends on feed purity, make up gas flow rate and energy requirements, etc. General ammonia synthesis loop it

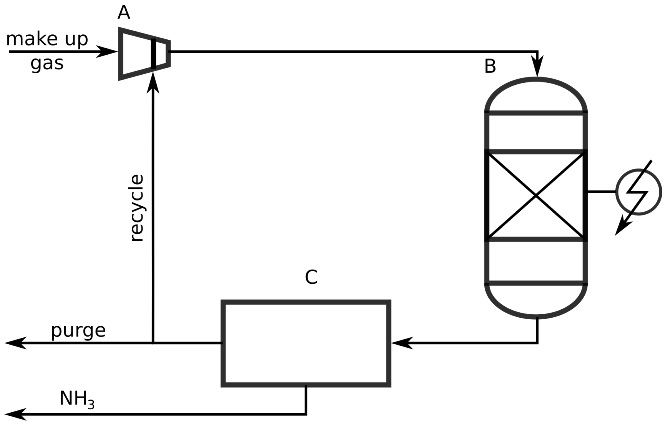
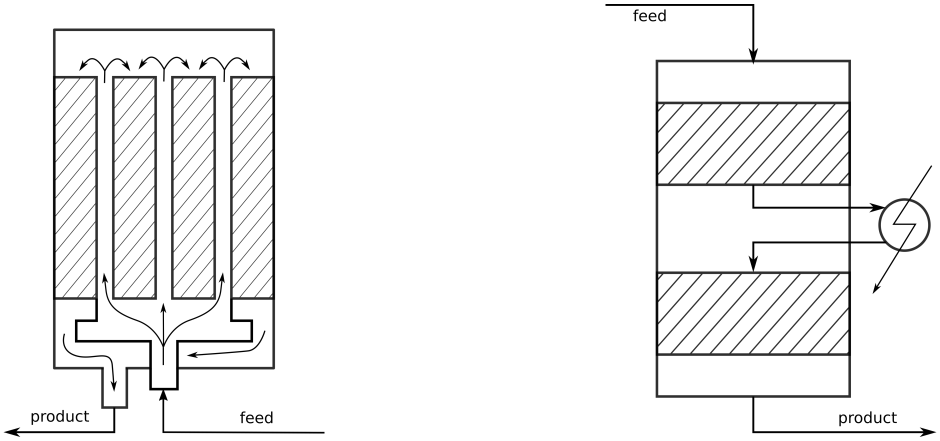


Figure 1.3: Ammonia synthesis loop
A: make up gas compressor, B: ammonia synthesis converter with heat recovery network, C: ammonia separation and refrigeration.

arranged as shown on Fig.1.3.[1]

Converter is a heart of the system, as it mainly defines operating conditions and provides yield of ammonia. Converter-wise, a number of different designs have been developed. They can be divided into two groups - with *internal bed cooling* (Fig. 1.4(a)) and *adiabatic bed* (Fig. 1.4(b)) converters with external heat exchange.[1] In former, a cold medium - usually make up gas - is running through the tubes to remove excess heat from the bed as well as to pre-heat feed and bring it up to the reaction temperature. Converters of these design have been widely used decades ago and more suitable for smaller scale production. Converters with multiple adiabatic beds are more wide spread in industry. Mainly, they can be divided into two groups based on method of heat removal. First is *quench cooling*, where hot gas effluent from each bed is cooled down by direct injection of colder stream. Second, *indirect cooling* of hot stream in separate waste heat boilers in order to generate steam needed for operation at ammonia plant or in heat exchanger to preheat converter feed. They are usually comprised of 2-4 beds and utilize axial or radial flow pattern. Beds with axial flow are more widely found, but on a number of modern plants converters have been redesigned into radial gas flow. It allows to reduce pressure drop across a bed and increase converter throughput within the same unit geometry.[11]



(a) Internal bed cooling (b) Adiabatic bed

Figure 1.4: Two principle designs of industrial ammonia converters

1.3 Overview of optimization methods

Optimization in engineering is aimed for the search of the “best” solution for a specific problem. Criteria to determine whether the solution is the “best” or not are varied widely and defined by an engineer (researcher) based on their experience, problems objectives, common sense, etc. For example, while optimizing performance of synthesis reactor its often desired to maximize possible yield of final product; or in the case of equipment design, it is common to reduce the total cost while keeping units performance at the desired level.

Engineering optimization can be classified by the number of objectives into single objective optimization (SOO) and multi-objective optimization (MOO). SOO approach has longer history. Essentially, it is based on formulation of unified function which represents the overall effect. Most of objective functions in SOO are related to economic efficiency of the process or unit. A classical example is optimization of insulation thickness. Insulation saves money through reduced heat losses but insulation can be highly costly at the same time. One has to compare total cost of insulation with savings from energy losses to find optimal thickness; the ratio between these two factors can be an objective

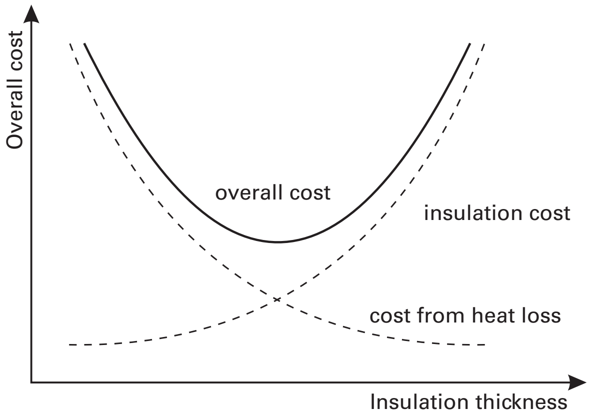


Figure 1.5: Overall economic effect of heat insulation

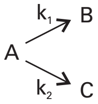


Figure 1.6: Parallel reaction scheme

function to be minimized (Fig. 1.5). It can be said that SOO methods are mainly aimed for search of an extreme point (minimum or maximum) in a search space.

However it is not always possible to formulate single objective for a particular problem which can adequately represent a meaningful optimal solution. MOO methods arise to overcome this drawback. One can deal with more than one objective and these objectives are not necessarily economic-related parameters. For example, consider a very common reaction engineering problem simultaneous yield maximization of goal (desired) product and minimization of undesirable side product. Such case is quite common for oil refining, petrochemical and polymer industry, organic synthesis, etc. Consider a simple parallel reaction, where we are targeting species B (desired) while species C is a side product (undesired) (Fig. 1.6):

Operating conditions might have similar effect on yield of both products, e.g. increase in process temperature increase percentage of both, desired and side, products in outflow. Plotting this trend (concentration vs. temperature) (see Fig. 1.7), it is possible to visualize conflictive nature of our objectives, that is one cannot increase concentration of B (desired) and decrease concentration of C (undesired) simultaneously. If we apply

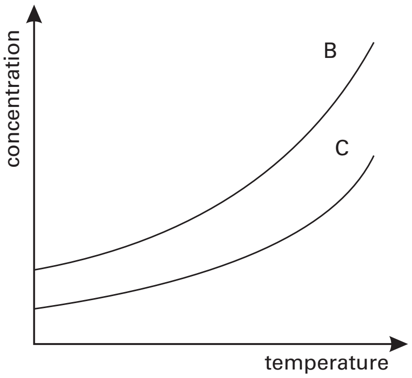


Figure 1.7: Effect of temperature on concentration of species in parallel reaction scheme

a classical single-objective approach, we would probably formulate objective function in some way relating price of production to concentrations of species. But, this type of objective function (cost minimization or profit maximization) usually is time- and/or site- specific. The cost of raw material or revenue generated from selling a product is site dependent (price varies from one region to another around the globe) and time dependent (price varies from year to year).

Application of MOO methods allows for solving such problem wherein one can directly treat product concentrations as objectives instead of single objective function expressed in terms of economic effect (cost minimization or profit maximization). This is why multi-objective approach is superior to classical Single objective approach.

Below, we will briefly consider the general ideas and concepts in use for MOO, describe methods, especially more recent and state-of art ones and make a review of their applications in chemical reactor engineering.

1.3.1 Multi-objective optimization

Concept of Multi-objective optimization

Multi-objective optimization (MOO) concept originates from economics and was developed by Italian economist, engineer and philosopher Vilfredo Pareto. At first let us consider the definition of multi-objective optimization of minimization problem (here and throughout the chapter we will discuss minimization MOO problems, since any maximization problem can be converted into minimization one easily):

$$\begin{gathered}\underset{x\in\mathbf{S}}{\text{minimize}} \quad I(\mathbf{x}) = [I_1(\mathbf{x}), I_2(\mathbf{x}), ..., I_n(\mathbf{x})] \\ \textit{subject} \quad \textit{to} \\ g_k(\mathbf{x}) \leq 0, \quad i = 1, 2...K \\ h_j(\mathbf{x}) = 0, \quad j = 1, 2...J \end{gathered} \tag{1.4}$$

General solution for such optimization problem is set of points, not a single one unlike in SOO problem. However, in some special cases, single point solution is also possible, this is a trivial case and is not considered. The set of points is called Pareto set (front or distribution).

Definition of Pareto Optimal Point: A point x is called Pareto optimal point if and only if there does not exist such point x^* in a search space that $I_i(\mathbf{x^*})$ is better than $I_i(\mathbf{x})$ for all objectives simultaneously. By better it is necessary to assume mathematical operators or depending on particular problem formulation.

Pareto set can be presented in terms of decision variables (set of x) or objectives (set of **I (x)**). For better understanding lets illustrate Pareto concept on two objective function problem. (Fig. 1.8) If the problem requires simultaneous maximization of both objectives A and B, Fig. 1.8 describes Pareto set obtained with respect to decision variable limits and equality and inequality constraints. If we move from point 1 to point 2, objective A is increasing (desired) while objective B is decreasing (undesired). It is said that these two points like any other points on the curve are non-inferior (non-superior or equally good) to each other. If we move from point 3 in the direction of Pareto, one can see that both objectives A and B are improving, thus point 3 is not a Pareto point.

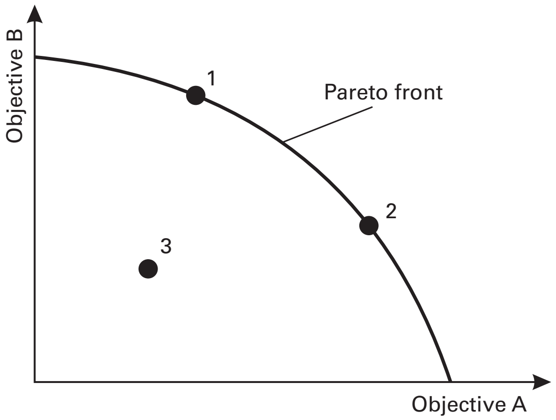


Figure 1.8: Pareto set for two conflicting objectives

1.3.2 MOO methods

Once solution for MOO problem in the form of Pareto set is defined, let turn one's attention to methods utilized for its search. There are number of different techniques; later the accepted classification will be provided for better understanding.[12–14] The classification is based on decision makers (DM) role in optimization search. Here DM is a person familiar with formulated problem; he/she can impact on preference of objectives or solutions. Therefore, methods are divided into:

- no-preference
- *a priori*
- *a posteriori*
- interactive

The first group excludes any influence of DM on search of Pareto points while next two take it into account. The latter case is a group of currently developing methods where DM is directly involved in optimization search and able to alter preferences until the best solution is found. Just note here as a remark that the classification is not strict because the same methods can be referred to by more than one group, this will be shown later. From here we provide further a concise review of introduced methods.

No-preference methods

If preferences are hard or impossible to define by DM, no-preference methods can be applied. They allow finding average solution regardless of any preference; no extra knowledge has to be provided by DM to solve such MOO problem.

Neutral compromised solution

Neutral compromised solution method allows finding optimal solution somewhere in the middle of Pareto set. To apply this technique it is required to define the norm in objective domain, which will be a measure of distance for middle solution, select a reference point from which the distance shall be minimized.[15] However we can say that DM expresses preferences by choosing the norm and reference point, but he/she is not doing it in explicit way. For MOO problems it is necessary for all objectives to be of the same dimension or dimensionless. The commonly used norms are p-norm, Chebyshev norm or augmented Chebyshev norm. The following problems are to be minimized respectively:

$$
\begin{gathered}
\underset{x \in \mathbf{S}}{\text{minimize}} \quad \left[\sum_{i=1}^{n} \frac{|I_{i,up} - I_i|^p}{|I_{i,up} - I_{i,low}|^p} \right]^{1/p}, \quad 1 < p < \inf \\
\underset{x \in \mathbf{S}}{\text{minimize}} \quad \max_{1 \le i \le n} \frac{|I_{i,up} - I_i|}{|I_{i,up} - I_{i,low}|} \\
\underset{x \in \mathbf{S}}{\text{minimize}} \quad \max_{1 \le i \le n} \frac{|I_{i,up} - I_i|}{|I_{i,up} - I_{i,low}|} + \epsilon \sum_{i=1}^{n} \frac{|I_{i,up} - I_i|}{|I_{i,up} - I_{i,low}|}
\end{gathered} \tag{1.5}
$$

Also, the Method of global criterion is one of such methods but will be considered in section of *a priori* methods below with some remarks.

A priori methods

A priori methods require DM to state his preference in MOO problem. This has to be done prior to determining the Pareto set. One can specify the priority of objectives (or aims) to be achieved. Since a DM is a person familiar with particular problem sometimes it becomes possible to single out more important objectives or put them in preference order.

Method of Weighted global criterion

This method with some variations is the most popular technique for MOO. The idea is to transform objective functions into a single one thereby scalarizing the search space. In the most general form this method can be written as:

$$\underset{x \in \mathbf{S}}{\text{minimize}} \quad \sum_{j=1}^{n} F(I_j(x), w_j) \tag{1.6}$$

A scalarized function represents the sum of composite functions of objective $\mathrm{I_i(x)}$ and weighting factor wi. The latter itself is a measure of DMs preferences on a particular objective. Usually weighting factors are assigned in such a way that $\sum w_j = 1$ and $w_j > 0$. In a simplest form expression 1.6 can be written as weighted exponential sum[14]:

$$\begin{aligned} &\underset{x \in \mathbf{S}}{\text{minimize}} \quad \sum_{j=1}^{n} w_j \left[I_j(x)\right]^p, \quad I_j(x) > 0 \\ &\underset{x \in \mathbf{S}}{\text{minimize}} \quad \sum_{j=1}^{n} \left[w_j I_j(x)\right]^p, \quad I_j(x) > 0 \end{aligned} \tag{1.7}$$

Note that in the case of p = 1, it is called method of weighted sum and widely used in applied chemical engineering problems.[16]

Lexicographic method

Lexicographic methods require DM to sequentially organize objectives from 1 to N in terms of preferences.[17] The following problem has to be solved[14]:

$$\begin{gathered} \underset{x \in \mathbf{S}}{\text{minimize}} I_i(x) \\ subject \quad to \\ I_k(x) < I_k(x^*) \\ k = 1, 2 ... i - 1, \quad i = 1, 2 ... n \end{gathered} \tag{1.8}$$

where k is a function order in preference list, $I_k(x_k^*)$ is constraints limit received at k^{th} step. First objective in the list should be minimized with the original constraints. If the DM obtains single solution one can accept it as an optimum. If not, the new constraint $I_k(x_k^*)$ has to be accepted to keep the k^{th} objectives optimal values. The procedure continues with next objective function (e.g. second function in a list, third function in a list, etc.), until the optimum is reached.

In reality it is often difficult for DM to distinctly organize objectives in order of importance on account of MOO problem complexity. Another drawback with this technique is that in unique solution is often found before the best optimal solution is reached. It means that some of objectives are not taken into consideration at all.[13]

Goal programming

This method was developed by Charnes and Cooper.[18] The DM defines a set of goals $\mathbf{G}$ which should be achieved for each objective, $I_i(x)$. Even if all these goals are unattainable simultaneously, it is still desired to approximate as close as possible. It is proposed to minimize the distance between vectors $I(x)$ and $\mathbf{G}$. Weighted GP problem formulation is written as:

$$\begin{gathered} \underset{x \in \mathbf{S}}{\text{minimize}} \sum_{i=1}^{n} w_i \delta_i \\ \delta_i = I_i(x) - g_i, i = 1, 2 ... n \end{gathered} \tag{1.9}$$

The formulation of goal programming problem doesnt necessary require the solution to be Pareto optimal. The solution obtained can be referred to (a) efficient, (b) inefficient or (c) unbounded solution. Efficient solution belongs to Pareto front while inefficient solution can be improved for two or more objectives simultaneously. The latter case is a solution located too far from Pareto front.[19]

Setting goals to attain is clear approach for DM (unlike, for example, use of utopia point in global criterion method). However, the further procedure for optimum search is not necessarily easy, e.g., weights assignment can be more difficult. Some GP methods are combined with lexicographic method, where deviations are structured in preference order and then minimized. The DM has to be aware of all drawbacks of GP methods and choose proper technique for finding optimal solution.

***A posteriori* methods**

In contrast to other methods discussed so far, *a posteriori* method generates Pareto set first, when the DM is given the opportunity to choose acceptable ones. It is reasonable if the DM is unsure about his/her preferences or problem definition is vague about relative importance of objectives.

ϵ-Constraint Method

The ϵ-constraint method is a non-scalarizing approach. Original idea was reported by Yacov Haimes.[20] The more comprehensive explanation is provided at Chankong and Haimes.[21] It is proposed to solve the following n-objective problem 1.4 to define Pareto set:

$$\begin{gathered}\underset{x\in\mathbf{S}}{\text{minimize}} I_i(x)\\ subject \quad to: \\ I_m(x) \leq \epsilon_m, i = 1, 2...n \ m \neq i \\ g_k(\mathbf{x}) \leq 0, \quad i = 1, 2...K \\ h_j(\mathbf{x}) = 0, \quad j = 1, 2...J\end{gathered} \tag{1.10}$$

Note that any of the objective functions can be chosen to be minimized. Varying ϵ_m the Pareto set can be reached. It is reported by authors that current method can deal with non-convex problems. However, drawbacks still exist. The choice of ϵ_m is not easy for DM as well as the technique significantly increases computation time if total number of equations (objectives and constraints) is relatively high.

Interactive methods

As it follows from the name interactive methods require some sort of interaction between the DM and MOO algorithm. Initially, no *a priori* information is required, and the DM specifies some objective-related preference information during a search process.

Solutions in interactive methods move iteratively providing the DM with some new solution(s) and allowing re-specifying his/her preferences, if needed. Interactive methods outcome is one or more Pareto optimal solutions, but not the entire Pareto set. Generally, many other variations exist, which are kind of extension of classical methods described here with the way how DM should interact with algorithm. There is variety of such methods and we will not discuss it here providing only references on some original sources and reviews.

- Interactive Surrogate Worth Trade-off (ISWT)[21]
- Reference point methods[22]
- Non-differentiable Interactive Multi-objective Bundle-based Optimization System (NIMBUS)[23]
- Step method (STEM)[24]

1.3.3 Genetic algorithms

Genetic algorithms (GAs) are currently one of the most developing groups of methods in MOO. They are based on the mechanics of natural selection and natural genetics.[25] Here we would like to emphasize the power of GA and discuss it in more details. While genetic algorithms belong to a posteriori methods; we discuss GA in an individual sub chapter on account of its fundamental difference from methods discussed above.

Original idea was proposed by Holland[26] as an adaptation concept. Thereafter, Goldberg evolved this theory and formulated general regulations of GAs.[25] GAs has been developed intensively in recent years, but the main principles remain the same. As indicated by Goldberg, main distinctions from classical methods are:

- GA works with number of points (population) instead of a single one

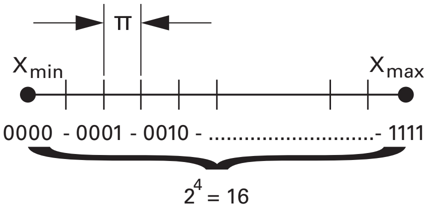


Figure 1.9: Mapping continuous variable into binary

- GA treats objective functions directly; there is no need for derivatives, utility functions, or any other auxiliary knowledge
- GA operators are probabilistic in nature in contrast to deterministic one used in all classical methods

GA is notable for its robustness. It is a superior search procedure in many aspects. Unlike many derivative-based methods that can be trapped around local optima, GA is a global optimum search procedure. It can also treat discontinuous or discrete functions. It overcomes issues with convexity of Pareto set as well as deals with multi-modal objective functions.[27]

About binary-coded variables

Preceding the explanation of GA working principles one have to know about binary-coded variables. The most common representation of a variable utilized by GA is a binary string. That variable simply is a certain length sequence of 1s and 0s (e.g. 1001). If user deals with continuous variable (e.g. length, product yield, time, etc.) it is required to discretize the variable. The procedure is quite simple. For example, decision variable $x \in [X_{min}, X_{max}]$ has to be mapped into binary string. User decides to use 4 bits for each variable, in other words, length of binary string l_{str} is set to 4 digits. Thereby, we have $2^4 = 16$ possible combinations of strings. Lower and upper bounds are assigned with values $X_{min} \rightarrow 0000$ and $Xmax \rightarrow 1111$. All the other values are mapped in between these two values. (Fig. 1.9) The precision of discretization of variable is directly

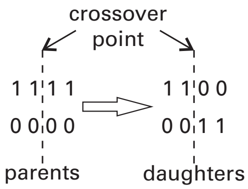


Figure 1.10: Genetic algorithm operator: crossover

dependent on the string length; more the length is, more binary variables can be mapped between lower and upper limit. Precision may be calculated as[25]:

$$\pi = \frac{x_{max} - x_{min}}{2^{l_{str}} - 1} \tag{1.11}$$

Simple Genetic Algorithm

For better understanding GAs principle lets consider simple genetic algorithm (SGA) first. The main components of SGA include a) reproduction, b) crossover and c) mutation genetic operators. At the beginning, initial population is generated randomly. The population is a set of individuals either of which represents a single decision variable (or a vector). The reproduction operator is applied on the population to create a mating pool. Individuals with higher objective function value have higher chance to be copied into a matting pool. Classical and simple way to perform reproduction operator is a roulette wheel[25].

Once the mating pool is formed, crossover and mutation operations are executed. In a single point crossover, two individuals (called parent chromosomes) are chosen randomly to exchange information with each other. They swap binary sequences after arbitrary position p (which is randomly selected) and generate daughter chromosomes. (Fig. 1.10)

Mutation is also aimed for altering the daughter chromosomes binaries but in a different manner. Like mutation in nature, it occurs with a very small probability. Mathematically it alters one cell in a sequence each time from 0 to 1 or vice versa. It is absolutely

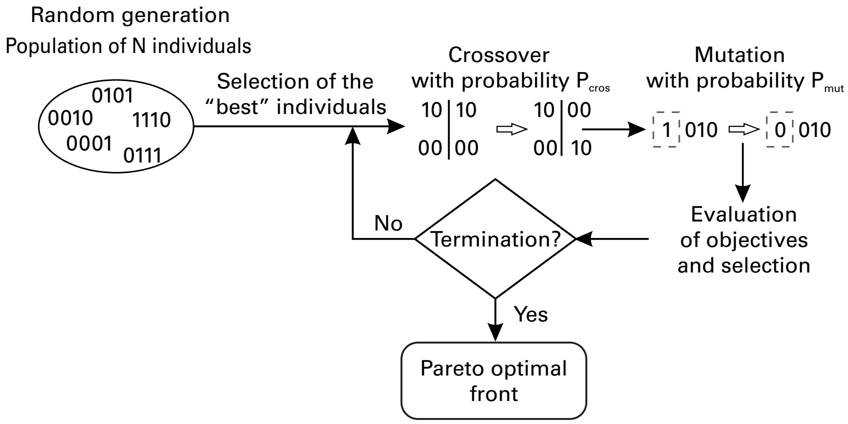


Figure 1.11: Genetic algorithm

necessary to keep diversity in population.[28] For example, lets assume a case where all individuals in population have 0 at k^{th} position, under this conditions crossover operator cannot create 1 there. Mutation allows overcoming this issue.

The best n daughter individuals are taken to form a new mating pool where crossover and mutation are carried out again. This procedure repeats until termination criterion is satisfied. Below we provide generalized scheme of SGA. (Fig. 1.11)

Use of GA in MOO

If one have SOO problem, it is easy to choose best solutions from the population by comparing single objective values of individuals. When one deals with multiple objectives, it becomes not clear how to compare them. To deal with this Goldberg introduces the concept of non-dominated vectors.[25] Vector $\boldsymbol{a}$ is said to be less than vector $\boldsymbol{b}$ if and only if these two conditions are satisfied simultaneously:

- all components of $\boldsymbol{a}$ are less or equal to corresponding components of $\boldsymbol{b}$
- at least one component of $\boldsymbol{a}$ is strictly less than corresponding element of $\boldsymbol{b}$

or in other words (for a minimization MOO problem) - $\boldsymbol{a}$ dominates $\boldsymbol{a}$. If for the vector a theres no such vector $\boldsymbol{c}$ that dominates it, vector $\boldsymbol{a}$ is called non-dominated. From this point of view a Pareto set is a non-dominated set.

I would like to emphasize one of the state-of-the-art algorithms non-dominated sorting genetic algorithm II (NSGA-II). Reader can note that this algorithm was used in majority of MOO problems solved in literature (Tab. 1). After development by Deb[29], it has been widely propagated in optimization problems for chemical engineering as well as for many other fields. NSGA-II is notable for its characteristics, especially ability to find diverse solutions close to real Pareto set and speed of convergence[29]. Here are elements which contribute to its high performance.

1. This algorithm uses concept of elitism. After mating pool formation, N parents and N daughters chromosomes are united into a single group of 2N. Selection is carried out over this pool and not only from the original mating pool. If parents are better than their daughters, it permits not to exclude them from population, but carry on in the next generation. This allows diversity.

2. Non-dominated Sorting Approach is used as a selection procedure. It divides entire population into groups of non-dominated individuals (*non-dominated fronts*). Any solution in front 1 is superior to any solution in front 2, and so on.

3. To maintain diversity of population, authors introduced crowding distance. If some region in objective domain is too populated with individuals it is reasonable to exclude some of them from population. Crowding distance of point i represents an average side length of n-dimensional cuboid in objective space, drawn out around point i where two neighbouring points are taken as vertices. The higher the crowding distance the less crowded a region. Points from the same front but with less values of this parameter have less chance to carry on into next generation. Step-by-step guide to execute NSGA-II, performance of algorithm in test problems or other characteristics can be found in elsewhere[27,29]

Constraint handling in GA

There are different techniques aimed for constraint handling in GAs. Constraints impose extra conditions onto MOO problem, thereby limiting the search space. Based on this, solutions are divided into feasible and infeasible regions. Infeasible solution cannot be neglected in GAs in order to maintain diversity. Even if particular solution violates constraints, it should have a chance to remain in population in order to have a chance to move to a feasible region.[27] To do this many techniques evaluate extent of violation from feasible region. Below two noteworthy techniques are discussed, which have been utilized more frequently while solving applied MOO problems in chemical engineering.

Penalty function approach Penalty function approach modifies original objective functions by adding a constraint violation to them as follows[28]:

$$\underset{x \in \mathbf{S}}{\text{minimize}} P(x) = I_i(x) + \Omega(R, g(x), h(x)) \tag{1.12}$$

Penalty term represents sum of constraint violations $v_i(x)$ from feasible region:

$$\Omega = R \sum v_i(x) \tag{1.13}$$

Constraint violations $v_i(x)$ are defined as:

$$v_i(x) = \begin{cases} |g_k(x)|, & g_k(x) \leq 0 \\ 0, & otherwise \end{cases} \tag{1.14}$$

or

$$v_i(x) = |h_i(x)|^2$$

Penalty parameter R is used to have values $I_i(x)$ and Ω of similar magnitude. Hence, if particular solution overruns feasible region, value of penalty function $P(x)$ increases even if the value of original objective function $I_i(x)$ is small. The solution becomes inferior and has higher chance to be excluded from population. One of the main drawbacks of this method is that penalty function distorts Pareto front of original function which cause difficulties finding true Pareto set.

Constrained Tournament Method

Constrained tournament method is a methods developed for use with GAs only. The approach can treat constraints directly instead of using any objective function transformation. It modifies the tournament selection of individuals for formation of mating pool. Now solutions are checked for constraint violation in addition to dominance. Between two infeasible solutions the one chosen is the one with less constraint violation. When two individuals are picked for tournament selection, the following *constraint-domination* rules have to be kept:

- Feasible individual is always superior to infeasible
- Between two infeasible individuals the one with smaller constraint violation should be given priority
- If both individuals are feasible the regular (non-constraint) approach should be applied

The generic *constraint-domination* principle can be used with any GA and does not require extra computational time[27].

1.3.4 Simulated annealing

Simulated annealing (SA) is another stochastic-based method of search and, like GAs, belongs to a posteriori methods. The procedure mimics the behaviour of molten metals cooling. At high temperatures, metals behave like a liquid where atoms are in chaotic motion. When the cooling is started, atoms lose mobility and begin to form crystalline lattice of solid metal. The rate of cooling strongly affects the structure of crystal, the slower the rate, the more uniformed the structure. Uniformed mono-crystalline structure has more stable (i.e. has minimum energy).

SA for optimization was first considered in Kirkpatrick et al.[30]. They applied principles of statistical mechanics of systems in thermal equilibrium to solve optimization problem. The main principle is based on Boltzmann probability distribution function. At given temperature T the probability of system to have energy E_1 is proportional to $exp(-E_1/kT)$, where k is the Boltzmann constant. In this context probability for a system to move from state 1 to state 2 is given as:

$$\frac{state1}{state2} = exp(\frac{-(E_2 - E_1)}{kT}) \tag{1.15}$$

Hence if E_2 is lower than E_1 when system definitely turns to state 2. At the same time, if $E_2 - E_1 \geq 0$ finite probability for transition from 1 to 2 still exists. The higher temperatures T correspond to higher probabilities of state 2 to exist. For energies in Boltzmann distribution equations, the reader has to consider objective values. SA in the simplest form can be described in the following way: the algorithm starts with an initial point x_0 (usually random). The random point x_1 is generated in the neighbourhood of x 0 and the objective values are compared at these points. If a new point improves our objectives, it is accepted instead of x_0. If not, the point x_1 is accepted with the probability $exp((E_2 - E_1)/kT)$. During the search, the temperature T is slowly decreased (cooling) which reduces the probability of a new point with worse objective being accepted. The search continues until some termination criteria are reached, for example, it can be an error between points in subsequent iteration or minimal temperature. One run of SA yields one Pareto optimal solution. Thus multiple simulations are required to obtain a Pareto set.

The same principle with some modifications can be applied for MOO problems.[31? –33] Algorithms could differ in probability functions or stopping criteria, or they have some operators for a better Pareto distribution. The current technique is less popular than GAs but still has a significant interest in modern MOO applications.

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Chapter 2

First principle modelling of an industrial ammonia converter

Nomenclature

α	constant parameter for reaction equation
α_i	convection heat transfer coefficient for interchanger [W/m^{2}K]
ν_i	stoichiometric coefficient in Eq. 2.1 for component i
χ	nitrogen conversion
ω	dimensionless distance from pellet center to interior point
ΔH_R	enthalpy of reaction [kJ/kmoleK]
ϵ	bed voidage
ϕ_i	fugacity coefficient of component i
η	effectiveness factor
C	total concentration of components [kmol/m^3]
C_p	specific heat capacity [kJ/kgK]
D_{ie}	effective diffusivity of component i [m^2/s]
f_i	fugacity of i$^{\text{th}}$ component
F_{N_2}	molar flow rate [mol/s]
K	overall heat transfer coefficient [W/m^{2}K]
k_2	kinetic constant of reverse reaction [kmol/m$^3 \cdot h$]
K_a	equilibrium constant
L	interchanger length [m^2]
l	length coordinate for interchanger [m^2]
$\dot{m}_i$	mass flow rate [kg/s]
P	pressure [Pa]

Q_i	volumetric rate [m^3/s]
r_i	tube radius [m]
R_{NH_3}	rate of ammonia formation [$kmol/m^3 \cdot h$]
R_p	radius of catalyst particle [m^2]
T	temperature [K]
V	bed volume [m^3]
X_i	molar fraction of component i

2.1 Introduction

Ammonia is one of major chemicals produced in the industry. It has a variety of applications: for manufacturing of inorganic salts, polymer fibers, explosives, etc. Its biggest role it plays for agricultural fertilizers: as an intermediate in urea production or used directly as liquid. It is hard to diminish the importance of ammonia for agricultural sector all over the world.[1]

Moreover, ammonia market is continuously growing. Total world ammonia demand has been steadily increasing over last decade at rate of 2.2 % per annum. One of the ways to satisfy for the demand is to boost up the performance of existing units through the comprehensive optimization.

One possible way this to be done is through first-principle mathematical modelling and numerical optimization. Developing robust models allows for accurate process simulation. Therefore, one can perform a comprehensive study of a process without expensive physical modelling and/or use the model for the numerical optimization to boost up process performance.

Modelling of ammonia synthesis has been drawing attention over the years and a number of attempts has been made. Baddour et al.[2] developed a simple one-dimensional plug-flow model for autothermal ammonia converter. They studied effect of process parameters such (*i.e.* feed temperature and composition) on ammonia production rate and temperature profile along catalyst bed. Shah[3] discussed two-bed adiabatic model with recovery heat exchange for the process control. He found best stable operating point as balance between heat generation and consumption. Gaines[4] used mathematical model for adiabatic bed with empirical correlation for effectiveness factor to perform analysis on model parameters. Singh and Saraf[5] modelled converters with both types - adiabatic and non-adiabatic - catalytic beds. They used pseudo homogeneous model with effectiveness factor based on reactants diffusion. Mansson and Andresen[6] did an optimization study for tubular ammonia converter with one-dimensional pug low model aiming to maximize ammonia content in the effluent and obtain optimal temperature profile. Elnashaie et al.[7] compared the performance of homogeneous and heterogeneous models for auto-thermal converter showing advantages and better accuracy for the latter. In the consequent works of *Elnashaie et al.*[8–10] they incorporated rigorous model for intraparticle diffusion and obtained more accurate solution for the effectiveness factor. They validated the model with data of Singh and Saraf[5]. Later, Upreti and Deb[11] performed a design optimization study with genetic algorithm by maximizing overall economic return of the synthesis having total converter length as a major decision variable. Babu and Angira[12] performed a similar study but could obtain more stable model solution in wider temperature range.

Summarizing, one can say that, firstly, it is evident that the topic still bears its value and importance. Models vary in complexity: some works consider broader range of units (as converters and product separators) in a model while others mainly consider converter itself. Secondly, models for different converter designs have been done (auto-thermal or adiabatic catalyst beds with different type of heat exchange). Each of studies shows that converters of different design distinct in optimal operating parameters, thus each particular converter arrangement bears different behaviour and requires independent investigation for the best results. Thirdly, some works focus on modelling for investigation of the process parameters effect on process performance while others perform more comprehensive optimization studies striving for higher ammonia production or least cost. However, none of the works, to the best of the author's knowledge, utilizes multi-objective optimization principles and performs optimization search for more than one objective. Hence, it could be beneficial for the complex system as industrial converter.

In this work we develop a first-principle mathematical model of an industrial ammonia synthesis converter with design not reported before. The model incorporates heterogeneous reaction kinetics with intra-particle diffusion resistances. As process being highly exothermic, the heat recovery model is also embedded into the overall converter model.

The model is able to predict gas temperature and concentration profiles along converter's bed, and the amount of heat which is recovered from a gas stream and recycled to supply for the pre-heat.

2.2 Overview of industrial ammonia synthesis and converter internals

Industrial ammonia synthesis is done through Haber process (see more detailed description below). There are a number of different technologies available for commercial application (*i.e.* Kellog, Haldor Topsoe, etc.). Regardless of any particular one, ammonia is produced through stoichiometric reaction of hydrogen and nitrogen (Eq.2.1). The reaction is slow at ambient conditions as well as limited by equilibrium, thus to achieve significant yields is carried out in a presence of catalyst under elevated temperatures (350 - 500 °C) and pressure (100-250 atm.)

Typical ammonia synthesis loop is presented on Fig. 2.1. Makeup gas coming from upstream units passes through loop compressor and forward to a synthesis converter. As hydrogen usually being produced upstream by steam conversion of methane, the makeup gas contains inert components (as methane, argon). Along with others, minor part of ammonia is also present among reactants. An ammonia-rich converter effluent (15-20 %

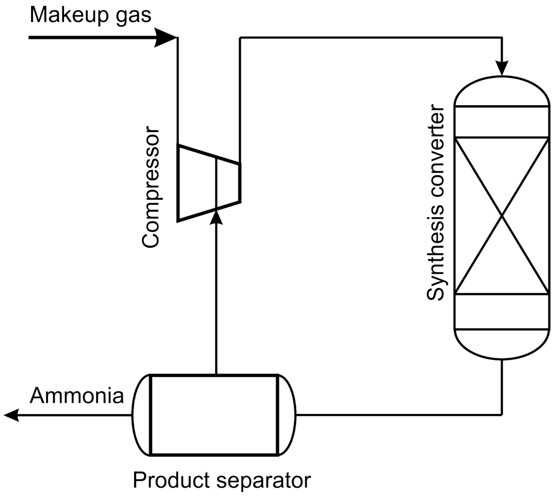


Figure 2.1: Ammonia synthesis loop

vol. ammonia) is sent to a separator where ammonia is separated into product stream while unconverted gases are recycled back to the compressor.

An ammonia converter is comprised of multiple (usually, three) fixed catalytic beds. Pre-heated gas stream enters a catalyst bed (Fig. 2.2). The synthesis reaction occurs on a surface and inside the pores of catalyst. While gas mixture heats up while passing along a bed. To prevent catalyst from exposure to high temperatures and shift reaction equilibrium the excess heat is removed. It is done in many ways: quenching, indirect heat exchange with cooling water or product stream, etc. Therefore, it is necessary to consider all those steps in order to develop an accurate mathematical model.

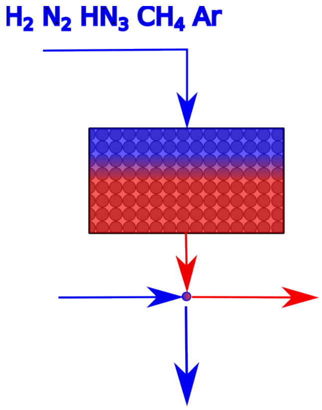


Figure 2.2: Schematic representation of a catalytic bed in ammonia converter

The ammonia converter to be modelled in this work is a three bed converter with heat interchanger and quenching. The converter's layout is provided in Fig. 2.3. Preheated and compressed synthesis gas is split into two flows - for main inlet and quench - in ratio tentatively 60/40.[1] The main feed enters from the bottom of reactor into annular space between outer shell and inner bed casing. It flows upwards to shell-side inlet of interchanger where the gas heats up to the reaction temperature by indirect heat exchange with effluent from second bed. The heated gas travels through the gap between interchanger and catalyst baskets up and enters first bed. The converter has the ability to quench prior to the first bed, but usually is done at start up only. At steady-state operation first bed quenching is relatively low or completely off. After first bed the main stream is quenched and enters next bed. The effluent from second bed passes through the tube-side of the interchanger into the third bed and out of the converter.

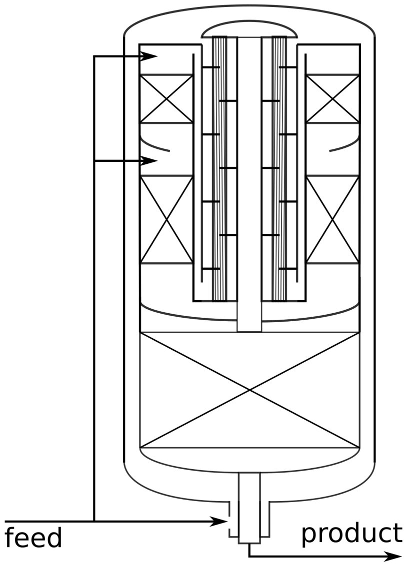


Figure 2.3: Internals of the ammonia converter

2.3 Converter modelling

Considering the process description and converter layout, the following assumption are made for converter modelling:

1. **Steady state operation**
2. **Adiabatic catalyst bed** The converter and catalyst basket are well insulated, therefore the heat transfer from reaction zone towards the gas flow is negligible.
3. **Negligible heat and mass transfer resistance at boundary of bulk and catalyst pellet** due to high gas velocities and bulk thermal conductivity.
4. **Significant diffusion resistances inside catalyst pellet**
5. **Constant temperature inside catalyst pellet** Due to high heat conductivity of catalyst support, the temperature profile inside a pellet can be assumed flat.
6. **One-dimensional plug flow model** Radial dispersion of mass and heat can be neglected for the well-insulated beds as well. Moreover, since we are not aiming to rigorously study gas flow patterns inside catalyst bed, it is reasonable to use one-dimensional model for global optimization of converter performance[3].
7. **No axial dispersion term** Ammonia converter bed is a gas solid system. Gas velocities are quite high and bulk viscosity is relatively low resulting in high Peclet number. Therefore, dispersion term can be neglected as well[13].
8. **Converter pressure is constant along converter** As reported in literature and observed by author from industrial data, the actual pressure drop along one bed is approximately 0.2 atm. Considering high loop pressures (100-250 atm.) this difference is negligible.

2.3.1 Ammonia synthesis reaction

Industrially ammonia is synthesized through the exothermic reaction of nitrogen and hydrogen in presence of catalyst (most often, iron-based) as shown by reaction:

$$N_2 + 3\,H_2 \longleftrightarrow 2\,NH_3, \quad \Delta H^0_{298} = -46.22 \quad \text{kJ/mol} \tag{2.1}$$

Even though the process has a long history and been extensively studied, there is still no consensus regarding the mechanism of the reaction over the catalyst. Therefore, a number of mechanisms as well as kinetic equations are found in the literature.[14–18] The Temkin equation (Eq.2.2) is found to be most widely used due to its accuracy and applicability:

$$R_{NH_3} = k_2 \left[K_a^2 f_{N_2} \left(\frac{f^3_{H2}}{f^2_{NH_3}} \right)^{\alpha} - \left(\frac{f^2_{NH_3}}{f^3_{H_2}} \right)^{1-\alpha} \right] \tag{2.2}$$

where R_{NH_3} - rate of ammonia formation [kmol/m^3·h], k_2 - kinetic constant of reverse reaction [kmol/m$^3 \cdot$ h], K_a - equilibrium constant, f_i - fugacity of i$^{\text{th}}$ component, α - constant number. The respective value for $\alpha = 0.55$[9] while k_2 is estimated with industrial data. The expression for equilibrium constant K_a is taken from[19] (Eq. 2.3):

$$logK_a = -2.691122logT - 5.519265 \times 10^{-5}T + 1.848863 \times 10^{-7}T^2 + 2001.6/T + 2.6899 \tag{2.3}$$

where T - process temperature [K].

Fugacity of i^{th} component is found as:

$$f_i = \phi_i X_i P \tag{2.4}$$

where ϕ_i - fugacity coefficient of i^{th} component, X_i - molar fraction of i^{th} component in gas stream, P - loop pressure [Pa].

2.3.2 Intraparticle diffusion

Industrially ammonia is synthesized over a variety of catalysts. Historically, first catalysts have been iron based and constitute majority of catalysts in use until now[1], however Ru-based catalysts have been commercialized in past decades, being more active yet expensive[20]. Whichever catalyst type is loaded in converter, it is usually in a form of pellets 4-10 mm in diameter. In order to provide larger surface, active component is immobilized on Al_2O_3 support. Due to porous structure of the support, diffusional resistances inside pores play significant role in integral synthesis reaction rate, therefore it has to be accounted for[21].

Assuming Fick-type diffusion, the mass balance for species i in spherical catalytic particle can be written as:

$$\frac{d^2X_i}{d\omega^2} - \left(\frac{2}{\nu_i + 2X_i}\right)\left(\frac{dX_i}{d\omega}\right)^2 + \frac{2}{\omega}\frac{dX_i}{d\omega} = - \left[\frac{R_p^2}{CD_{ie}}(\nu_i + 2X_i)\right]\frac{R_{NH_3}(X,T,P)}{1-\epsilon} \quad (2.5)$$

subject to boundary conditions:

$$\omega = 0: \quad \frac{dX_i}{d\omega} = 0$$
$$\omega = 1: \quad X_i = X_i(bulk)$$

where ν_i - corresponding stoichiometric coefficient in synthesis reaction (Eq. 2.1), ω - dimensionless distance from pellet center to interior point, R_p - pellet radius [m^2], C - total concentration [$kmol/m^3$], D_{ie} - effecitive diffusivity [m^2/s], ϵ - bed voidage.

The Eq. 2.5 is solved using orthogonal collocation method[22] using 4 collocation points. The solution yields a concentration profile for the reactants. Therefore, one can calculate the reaction rate at different radial positions and obtain effectiveness factor η as:

$$\eta = \frac{\int_0^1 \omega^2 R_{NH_3}(\omega, X, T, P) d\omega}{R_{NH_{3bulk}}(X_{bulk}, T_{bulk}, P_{bulk})} \tag{2.6}$$

2.3.3 Mass and energy balance of catalyst bed

For catalyst bed hydrodynamics model we adopt one-dimensional plug flow model. Therefore, differential mass and energy balance equations are written as:

$$\frac{d\chi}{dV} = \frac{\eta R_{NH_3}(\mathbf{X}, T, P)}{2F^0_{N_2}} \tag{2.7}$$

$$\frac{dT}{dV} = \frac{(-\Delta H_R)\eta R_{NH_3}(\mathbf{X}, T, P)}{\dot{m}_{gas} C_{p,gas}} \tag{2.8}$$

where ΔH_R - enthalpy of reaction at current temperature [kJ/kmoleK], χ - fractional conversion of nitrogen, V - catalyst bed volume [m^3], F_{N_2} - molar flow rate at bed inlet, $\dot{m}_i$ - mass flow rate of gas [kg/h].

2.3.4 Interchanger model

Interchanger located in the middle of converter is a shell-and-tube heat exchanger with axial flow(Fig. 2.4). It transfers heat effluent from second bed's hot effluent to the “cold” inlet synthesis gas stream. The synthesis gas is fed into shell, while effluent - into tube side.

By means of interchanger second bed effluent cools down while synthesis gas is bought up to the temperature just enough to start the reaction. The governing heat transfer

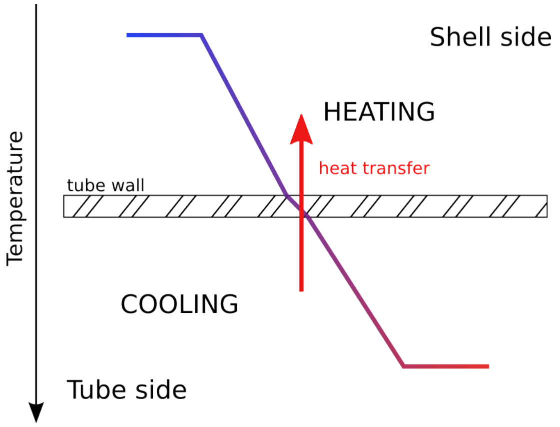


Figure 2.4: Heat transfer along tube wall

equation for the interchanger is:

$$\text{Shell side}: \tag{2.9}$$

$$\frac{dT_{shell}}{dl} = \frac{2\pi K(T_{tube} - T_{shell})}{\dot{m}_{shell} C_{p_{shell}}} \tag{2.10}$$

$$\text{Tube side}: \tag{2.11}$$

$$\frac{dT_{tube}}{dl} = -\frac{2\pi K(T_{tube} - T_{shell})}{\dot{m}_{tube} C_{p_{tube}}} \tag{2.12}$$

$$K = \left[\frac{1}{\alpha_{tube} r_{inner}} + \frac{1}{\lambda}\frac{1}{\alpha_{shell} r_{outer}}\right]^{-1} \tag{2.13}$$

subject to boundary conditions:

$$l = 0: \quad T_{shell} = T_{bed1}^{inlet}$$

$$l = L: \quad T_{tube} = T_{bed2}^{outlet}$$

where K - overall heat transfer coefficient [W/m^{2}K], α_i - convective heat transfer coefficient towards tube wall from shell or tube side [W/m^{2}K], r_i - inner or outer interchanger tube radius [m], λ - thermal conductivity of interchanger material [W/mK], l - length coordinate for interchanger integration [m], L - interchanger length [m]. Detailed model derivation for interchanger for a given geometry can be found in appendix A.

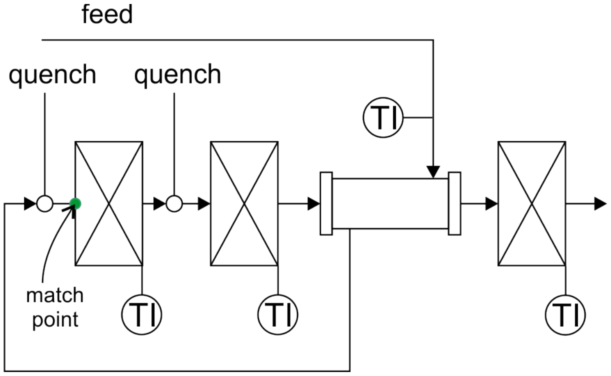


Figure 2.5: Simulation procedure for the ammonia converter

2.3.5 Model overview

The intraparticle diffusion is boundary-valuer problem and solved through transformation of equation into set of non-linear equation by orthogonal collocation with 4 collocation points. Then the system is solved by the Newton method. The catalyst bed mass and heat balance equations are solved as initial value problem using Runge-Kutta 5^th order method. The interchanger model is a boundary-value problem and solved using mono-implicit Runge-Kutta method (based on subroutine "bvptwpc"[23]). The simulation is carried out as shown on Fig. 2.5. The initial guess is set on inlet temperature for first bed, then the model is run in series for two quenching and beds followed by interchanger and checked whether shell side temperature at interchanger outlet matches initial guess. If error is below 10^{-5} then simulation follows to calculate the outcome of the third bed. Thus, the model yields temperature and gas composition profile along the converter length.

2.4 Results and Discussion

2.4.1 Model validation

As kinetic parameters of catalyst remain unknown, they were estimated using industrial data. In reality, the catalyst in each bed is a layered mixture of few catalyst brands of different activity and size in certain ratio. Therefore, the kinetic parameters in each bed are averaging the individual kinetic parameters of each of the catalysts. The sum of squared distances between observed and simulated temperatures for each bed is minimized in order to do model fitting:

$$min \quad \sum_{i=1}^{3}(T_{bed_i}^{simulated} - T_{bed_i}^{observed})^2 \tag{2.14}$$

To assess validity, one can compare temperatures between simulated profile and on bed boundaries, measured by thermocouples. One can find that the model proved a good overall match. The error for the most cases lies within few °C. Especially notable that simulated temperature for the first bed inlet is very close to measured one. Considering that the model of interchanger was excluded from fitting stage (see 2.14), but validation was carried out with interchanger on, it, first of all, validates assumption that heat losses from catalyst basket towards gas stream inside converter are negligible. Secondly, it ensures the validity of interchanger model as well, since we are unable to validate it directly and independently from the whole converter. The only largest observed error is for inlet into the third bed. This discrepancy might result from the fact that this temperature is not measured directly in a gas flow but taken as an average of three thermocouples located inside the third bed (Fig. **??**). Moreover, one can look into comparison of gas compositions in Table 2.1. Even though components concentrations were not included into fitting, but along with temperatures they have a close match.

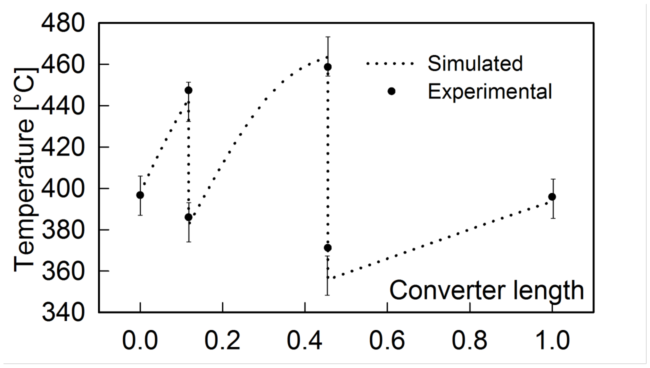


Figure 2.6: Comparison between simulated and observed temperatures along reactor

	Gas stream composition [% mol.]				
	N_2	H_2	NH_3	CH_4	Ar
simulated	23.53	56.38	13.31	5.08	1.70
experimental	23.10	56.50	13.56	5.08	1.71

Table 2.1: Comparison between simulated and experimented gas composition

2.4.2 Sensitivity analysis

The sensitivity analysis of the model was performed in order to *a)* check that model performs “as expected” (*i.e.* with agreement of thermodynamics, reaction kinetics, engineering sense) and *b)* evaluate effect of parameters onto process performance (Table 2.2). The analysis performed as follows: the most important process parameters were chosen and fixed at reference value (denoted by “-” sign). Then, parameter varies one at a time around reference in order to quantify its effect on performance indicators. The chosen process control parameters are: feed temperature T_{feed}, volumetric flow rate for converter inlet and quenches Q_i, loop pressure P, second bed’s quench-to-feed ratio $Q_{quench2}/Q_{feed}$. As performance indicators the following are used: outlet temperature from each bed T_i^{out}, conversion per bed χ_i, ammonia content in converter outlet X_{NH_3}, temperature change across interchanger from tube side ΔT_{tube}. The latter is chosen as a measure of heat recovery in the system, since it is proportional to the value. Thus, it is indirect measure of heat recovery efficiency.

The increase in feed temperature shows an increase in total ammonia production

Table 2.2: Sensitivity analysis

Parameter	Value		T_{bed1}^{out}	T_{bed2}^{out}	T_{bed3}^{out}	ΔT_{tube}	χ_{bed1}	χ_{bed2}	χ_{bed3}	X_{NH_3}
T_{feed}	+10%	266.26	457.03 ↑	468.44 ↑	411.81 ↑	98.60 ↓	5.53 ↑	9.04 ↓	5.41 ↑	13.40 ↑
	-	242.06	443.38	463.58	393.57	107.80	5.22	9.58	4.89	13.31
	-10%	217.85	247.31 ↓	456.77 ↓	372.82 ↓	116.03 ↑	4.79 ↓	10.08 ↑	4.16 ↓	13.04 ↓
Q_{feed}	+10%	65.56	434.52 ↓	461.72 ↓	389.30 ↓	107.96 ↑	4.67 ↓	9.62 ↑	4.59 ↓	13.01 ↓
	-	59.6	443.38	463.58	393.57	107.80	5.22	9.58	4.89	13.31
	-10%	53.64	452.62 ↑	464.60 ↑	397.89 ↑	106.91 ↓	5.82 ↑	9.52 ↓	5.21 ↑	13.61 ↑
P	+10%	96.83	457.99 ↑	473.27 ↑	405.22 ↑	112.31 ↑	6.12 ↑	9.55 ↓	5.75 ↑	14.12 ↑
	-	88.03	443.38	463.58	393.57	107.80	5.22	9.58	4.89	13.31
	-10%	79.22	423.61 ↓	447.82 ↓	378.86 ↓	100.37 ↓	4.21 ↓	9.32 ↓	4.03 ↓	12.29 ↓
$Q_{quench2}$	+10%	38.49	442.41 ↓	460.17 ↓	392.78 ↓	104.10 ↓	5.19 ↓	9.73 ↑	4.75 ↓	13.25 ↓
	-	34.99	443.38	463.58	393.56	107.80	5.22	9.58	4.89	13.31
	-10%	31.49	443.64 ↑	466.37 ↑	393.98 ↑	111.34 ↑	5.22	9.38 ↓	5.04 ↑	13.34 ↑
$Q_{quench1}$	+10%	3.4987	431.95 ↓	459.67 ↓	392.51 ↓	103.87 ↓	4.77 ↓	9.84 ↑	4.75 ↓	13.24 ↓
	-	0	443.38	463.58	393.56	107.80	5.22	9.58	4.89	13.31
$Q_{quench2}/Q_{feed}$	more	1.31	450.45 ↑	457.04 ↓	396.12 ↑	98.51 ↓	5.77 ↑	9.90 ↑	4.88 ↓	13.48 ↑
	-	1.70	443.38	463.58	393.56	107.80	5.22	9.58	4.89	13.31
	less	2.86	432.69 ↓	469.72 ↑	389.25 ↓	118.41 ↑	4.53 ↓	9.13 ↓	4.89 ↓	13.01 ↓

(X_{NH_3}) as a result of higher reaction rate on average, however individual conversions over bed does not simultaneously follow the increase. The second bed has lower conversion, but total increase is reached by means of first and third beds. At the same time, it lowers the efficiency of interchanger shown by lower ΔT_{tube} due to lower temperature gradient between tube and shell sides. Higher feed flow rates on opposite reduce space time hence reducing X_{NH_3}. But as in case with T, it is not reflected identically in all beds' conversion. On contrary, second bed gives boost in conversion while other two drop while counter effect is done on ΔT_{tube}. Higher pressure like feed temperature boosts up reaction rate yielding higher ammonia in reactor effluent. Higher quench like higher feed flow rate - either to first or second bed - both have similar effect on every process indicator due to reduction of space time. Notable, that heat recovery efficiency ΔT_{tube} and X_{NH_3} are showing different trends - if one increases other decreases and vice versa.

2.4.3 Effect of process parameters

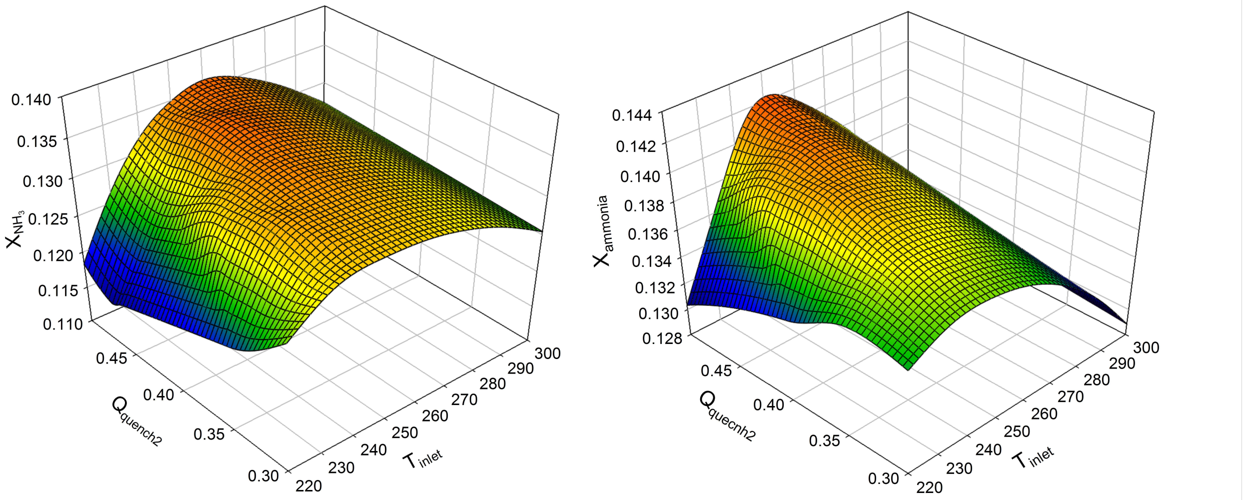
One can note that among considered process parameters, the largest effect on process indicators is delivered by three process parameters: T_{inlet}, P and $Q_{quench,bed2}/Q_{feed}$, while others have smaller impact. Although Q_{feed} also has large effect, but engineering-wise it is not easy to vary feed flow rate since it involves complicated alteration of operation mode on preceding series of units. Thus we had been mainly focused on these three to estimated their effect on process performance. Firstly, to carry out simulations have established decision domain in accordance with industrial practice. To set the range we have studied the process history for over 10 years and extended the range by 40 °C for feed temperature, by 10 % for quench-to-feed ratio, for pressure - we chose one value to represent lower and upper range(Table 2.3).

Table 2.3: Simulation range

Variable	Lower	Upper
T_{inlet}	220	300
$Q_{quench,bed2}/Q_{feed}$	0.3	0.5
P	85	91

Simulation results for effect on ammonia production and heat recovery are shown in Fig. 2.7 and Fig. 2.8 respectively. Firstly, one can see that for a given loop pressure variation of T_{inlet} and $Q_{quench,bed2}/Q_{feed}$ allow for wide range production rate - 12 to 13.8% and 13 to 14.2 % for 85 and 91 atm. respectively. Usually, acceptable production lies above 13% of ammonia in converter effluent, thus improper control might significantly drop X_{NH_3} below acceptable significantly reducing process efficiency. Secondly, T_{inlet} has a pronounced maximum for ammonia production (*i.e.* convex surface). More, at higher pressure (Fig. 2.7b) the convex peak is steeper. So, if higher production is needed a careful attention has to be taken for adjusting feed temperature. The effect of quench is mostly monotonous, favouring higher ammonia production at higher quench-to-feed ratios.

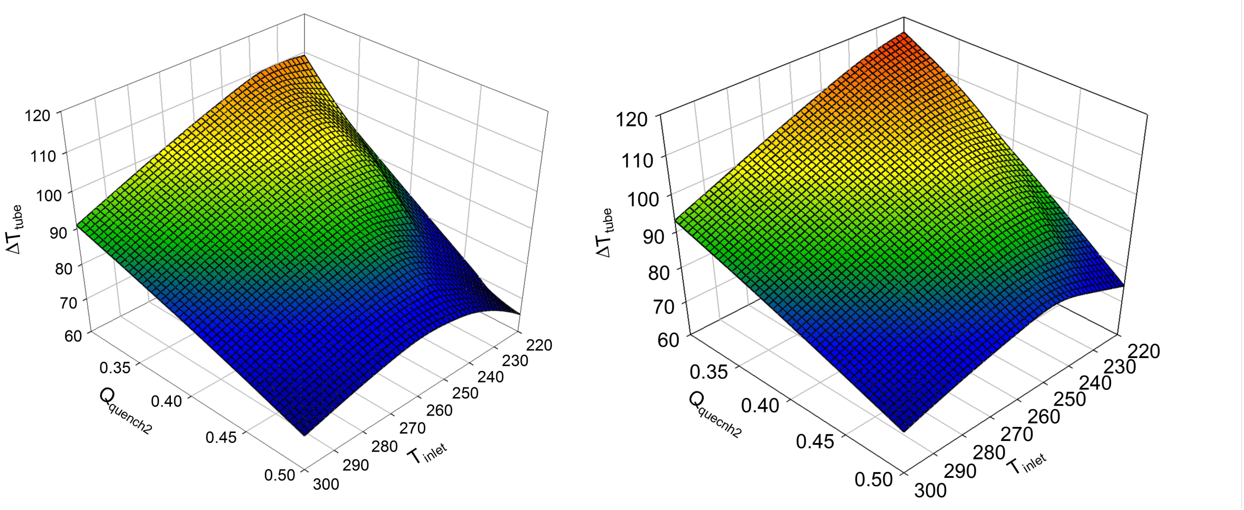
There is a different picture if one to take a look onto effect on heat recovery within the converter. Firstly, variation of these parameters allows for ΔT_{tube} change in range 70 to 120 °C. It is a significant variation of 40 %. Especially, considering the large scale of production this results in high absolute values for heat recovery. However, there's no engineering requirements for heat recovery during production, this is important to



(a) P=85 atm. (b) P=91 atm.

Figure 2.7: Effect of process parameters on ammonia production

consider because it is able to reduce overall heat duty for the converter. Secondly, heat recovery is more sensitive to quench-to-feed ratio than ammonia production. Although, there's an also convex maximum with respect to T_{feed} at higher ratio, but the heat recovery is more monotonous at lower quench and higher pressure. Moreover, in contrast to ammonia production, higher heat recovery is favoured by lower quench.



(a) P=85 atm. (b) P=91 atm.

Figure 2.8: Effect of process parameters on heat recovery

Therefore, a better process performance for ammonia production can be done by controlling three main parameters: T_{inlet}, P and $Q_{quench,bed2}/Q_{feed}$. They can cover a wide range of process operation and it is possible to improve performance by their proper adjustment. If one needs to increase ammonia content in converter effluent X_{NH_3}, then it is needed to find a "sweet spot" in controlling feed temperature. It is possible to significantly improve X_{NH_3} even without changing a loop pressure if for an engineering purpose it has to be kept constant. Quenching can also help to improve production, however its most effect it can influence on heat recovery. Unfortunately, higher heat recovery corresponds to lower ammonia production, thus it is necessary to decide on which mode is acceptable and efficient to properly set process control parameters for best outcome.

2.5 Summary and conclusion

Firstly, in this work we considered a model development for simulation of an industrial ammonia converter. Model includes four major parts: reaction kinetics, diffusion of reactants inside solid catalytic particle, model for fixed hydrodynamics and model for heat interchanger. The model was tested on a large scale industrial ammonia converter: model fitting and validation were performed using design parameters and operation data. The model found to have a good agreement with industrial data. From model sensitivity analysis we were able to conclude the most important parameters for process performance improvement. They are: feed temperature T_{inlet}, loop pressure P and quench-to-feed ratio $Q_{quench,bed2}/Q_{feed}$. We evaluated their effect on ammonia production X_{NH_3} and heat recovery within interchanger ΔT_{tube}. It was found that variation of these three allows for wide range of performance solutions. By their proper adjustment it is possible to achieve improved production rate or heat recovery. However, both performance indicators are in conflict - one cannot improve them simultaneously, hence needs to compromise.

Therefore, engineering judgment and/or additional performance priorities are needed to make a final decision about operational conditions.

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Chapter 3

Surrogate-based multi-objective optimization of the industrial ammonia converter with NSGA-II

Nomenclature

ΔH_R	enthalpy of reaction [kJ/kmoleK]
AIC	Akaike information criterion
bed	refers to catalyst bed
C	total concentration of components [kmol/m^3]
D_{ie}	effective diffusivity of component i [m^2/s]
f_i	fugacity of i$^{\text{th}}$ component
F_{N_2}	molar flow rate [mol/s]
$feed$	refers to process gas feed into the converter
HR	heat recovered through heat recovery system
k_2	kinetic constant of reverse reaction [kmol/m$^3 \cdot h$]
K_a	equilibrium constant
$\dot{m}_i$	mass flow rate [kg/s]
out	refers to a catalyst bed out
P	converter pressure [atm.]
Q	volumetric rate [m^3/s]
QFR	quench-to-feed ratio
$quench$	refers to converter quench
R_{NH_3}	rate of ammonia formation [kmol/m$^3 \cdot$ h]
R_p	radius of catalyst particle [m^2]
T	gas temperature [°C]
V	bed volume [m^3]

X_i	molar fraction of component i

Greek letters

α	constant parameter for reaction equation
ν_i	stoichiometric coefficient in Eq. 3.1 for component i
χ	nitrogen conversion
ω	dimensionless distance from pellet center to interior point
ϵ	bed voidage
ϕ_i	fugacity coefficient of component i

3.1 Introduction

Ammonia is one of major chemicals produced in the industry. It has a variety of applications: for manufacturing of inorganic salts, polymer fibers, explosives, etc. Its biggest role it plays for agricultural fertilizers: as an intermediate in urea production or used directly as liquid. It is hard to diminish the importance of ammonia for agricultural sector all over the world[1].

The use of rigorous mathematical models in process design and optimization has been extensively used for a large-scale chemical engineering processes. Model simulations allows for fast and accurate investigation of the decision domain providing an engineer/researcher with valuable knowledge on a process behaviour while avoiding expensive and time consuming lab scale or industrial experiments. Therefore, one can perform a comprehensive study of a process for the numerical optimization to boost up process performance.

Conceptually, there are two approaches in optimization - single and multi-objective (SOO and MOO respectively). The former formulates a sole objective function to be optimized into a single point solution, while latter treats two or more objective objective functions to find (likely) a set of equally good solutions.

However, SOO approach is still extensively used, but MOO has gained its popularity in chemical engineering. Large-scale industrial processes are very complex system, so often it is troublesome to single out the only objective. Thus, it is especially beneficial to use multi-objective approach for optimization of industrial processes.

Multi-objective optimization has been successfully performed in a number of works, especially in oil refining processes[2–7], steam reforming[8–13], polymer manufacturing[14–19] and hydrogen production[20–23]. All these works evidently showed advantages of multi-objective approach applied to industrial problems. The most common objectives are related to: *a)* production of the desired product, *b)* production of side or undesired products and *c)* utilities. Constraint-wise, problems usually have a few (mostly one to three) additional requirements for process conditions (*i.e.* upper or lower cap for stream temperature or composition). Problems are solved predominantly with multi-objective optimization methods, such as multi-objective genetic algorithms (*e.g.* NSGA-II[24]), multi-objective simulated annealing[25], however, some other problems are formulated through, for example, ϵ-constraint or objective sum method and solved as single-objective problem. The main outcome of the problem solution is obtained set (known as Pareto set) of non-dominating points, which resemble best solution with respect to all objectives. Additionally, they reflect the trade-off between objectives, thus illustrating whether one can significantly improve one objective while not worsening other beyond reasonable.

However, theoretically one can handle infinitely many objectives and constraints, the problems solved in the literature are mostly two and sometimes three objective. Firstly, it is worthwhile in terms of results interpretation as easier to visualize and analyze. Secondly, definition of overly complicated multi-objective optimization problem is excessive as one usually willing to find practically feasible solution. In industrial processes it is quite often not possible to adjust some parameters or measure process performance with high accuracy. Thus two or three objective problems are sufficiently enough in majority of cases in order to obtain a good set of solutions. If required to account for more objectives, they can be included as constraints.

Few attempts has been made to perform optimization study for an industrial ammonia synthesis by a number of authors(Mansson and Andresen[26], Elnashaie and Alhabdan[27], Upreti and Deb[28], Babu and Angira[29]). They aimed towards maximization of ammonia production or overall economic profit. To the best of authors knowledge, none of the works available in open literature treats the problem in multi-objective manner.

There is one more major problem related to process optimization. In order to perform numerical optimization one requires to run a number (and often quite large) of model simulations. Sometimes even a single simulation is computationally expensive, thus total optimization search will result in a large time. Imagine one uses NSGA-II with 100 individuals and 100 generations (however, in real search much larger number generations is needed). In case if a single simulations takes 1 minute, the most conservative estimate will be around 166 CPU-hours, and that excluding algorithm itself, taking into account simulations only. One of the possible ways would be a code optimization either for model or optimization algorithm. Firstly, the optimization is time consuming itself, and time spent may not be payed off by results of the search. As famous saying declare “premature optimization is a root of all evil”, thus one shall not strive for it without dire need.

Secondly, one can run model or optimization search in parallel thus decreasing elapsed time. It is efficient way, however, like in previous case, development-wise is also time consuming. One may need to find places within a model which can be efficiently parallelized. Also, parellelizing optimization search can boost up time while keeping the model’s code untouched. For example, any genetic algorithm requires a number of independent model evaluations at each generations. Thus, one can parallelize a model up to the number of available cores. In case of derivative-based optimization, one will be limited by the number of derivatives regardless of cores available. This all making an improvements in code performance non-trivial task, therefore one shall carefully decide if it is a worthwhile to do.

An alternative solution is to use surrogate model instead of original one for the optimization. Surrogate is a regression model obtained from a simulation data of original model[30,31]. With required accuracy it is resembled in behaviour but computationally much cheaper. Therefore, it can be used with existing optimization codes without any alteration, thereby saving development time. An optimization run even on a single-core will be much more faster. Optimization with surrogates have been successfully applied for chemical engineering problems. A number of works available in open literature solving optimization problems for chemical engineering tasks, e.g. optimization of distillation columns[32], design and optimization of chemical engineering units under uncertainty[33], flow sheet optimization[34], etc. It was shown that with use of proper surrogate it is possible to substitute original with proper regression model without loss of accuracy and obtain effective and feasible solution.

In this work, we utilize a developed first-principle model for an industrial ammonia converter. The model was validated with industrial data and showed a satisfactory accuracy. After, we trained a surrogate model with Eureqa®[35,36]. Then obtained regression model was coupled with optimization algorithm and few two-objective optimization cases have been solved. One can find a broad range of optimal solutions with a trade of between objectives.

3.2 Ammonia synthesis and model summary

Regardless of particular technology, industrial ammonia synthesis is done through Haber process. The ammonia is produced through the reaction of hydrogen and nitrogen:

$$\mathrm{N_2} + 3\,\mathrm{H_2} \longleftrightarrow 2\,\mathrm{NH_3}, \quad \Delta H^0_{298} = 46.22 \quad \mathrm{kJ/mol} \tag{3.1}$$

The reaction is carried out under elevated temperature and pressure to suffice significant yield. The Eq. 3.1 is a gas-solid reaction occurring in presence of iron or ruthenium

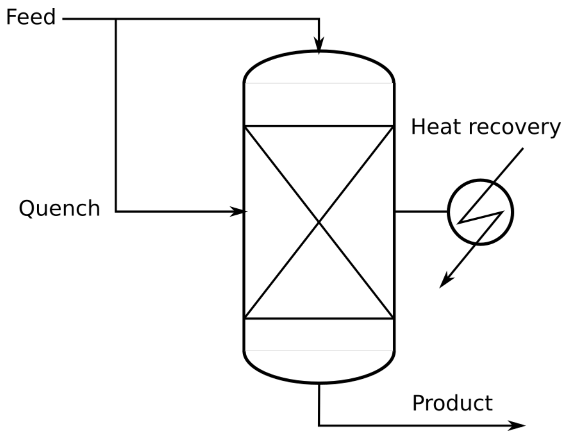

Figure 3.1: Ammonia converter schematic

catalyst. The catalytic ammonia converter is made of few packed beds. The reaction mixture is sequentially fed into beds to produced ammonia in steps. The intermediate cooling is essential as the reaction 3.1 is exothermic. To prevent catalyst from exposure to high temperatures and shift reaction equilibrium the excess heat is removed between beds.

The object of study is a three bed ammonia converter. The simplified layout is provided at Fig. 3.1. The synthesis gas is split into two flows - for main feed and quench. The main feed enters prior the first bed, while quenching is done in between. The process gas passes though a bed and experiences a temperature rise. This is where quenching and heat recovery is used - to remove the excess heat from the gas stream.

The main steps of ammonia synthesis in this reactor include:

1. Reaction kinetics
2. Intraparticle diffusion
3. Fixed bed hydrodynamics model
4. Heat recovery model

The four following steps were implemented in the model. The reaction rate is modelled by a Temkin equation:

$$R_{NH_3} = k_2 \left[K_a^2 f_{N_2} \left(\frac{f_{H2}^3}{f_{NH_3}^2} \right)^{\alpha} - \left(\frac{f_{NH_3}^2}{f_{H_2}^3} \right)^{1-\alpha} \right] \tag{3.2}$$

where R_{NH_3} - rate of ammonia formation [kmol/m^3·h], k_2 - kinetic constant of reverse reaction [kmol/m$^3 \cdot$ h], K_a - equilibrium constant, f_i - fugacity of i$^{\text{th}}$ component, α - constant number. Intraparticle diffusion is derived through mass balance assuming Fick diffusion[37]:

$$\frac{d^2X_i}{d\omega^2} - \left(\frac{2}{\nu_i + 2X_i} \right) \left(\frac{dX_i}{d\omega} \right)^2 + \frac{2}{\omega} \frac{dX_i}{d\omega} = - \left[\frac{R_p^2}{CD_{ie}} (\nu_i + 2X_i) \right] \frac{R_{NH_3}(X, T, P)}{1 - \epsilon} \tag{3.3}$$

subject to boundary conditions:

$$\omega = 0 : \quad \frac{dX_i}{d\omega} = 0$$

$$\omega = 1 : \quad X_i = X_i(bulk)$$

where ν_i - corresponding stoichiometric coefficient in synthesis reaction (Eq. 3.1), ω - dimensionless distance from pellet center to interior point, R_p - pellet radius [m^2], C - total concentration [kmol/m^3], D_{ie} - effective diffusivity [m^2/s], ϵ - bed voidage. The catalyst bed hydrodynamics is assumed to be a one-dimensional plug flow with no axial dispersion:

$$\frac{d\chi}{dV} = \frac{\eta R_{NH_3}(\mathbf{X}, T, P)}{2F_{N_2}^0} \tag{3.4}$$

$$\frac{dT}{dV} = \frac{(-\Delta H_R)\eta R_{NH_3}(\mathbf{X}, T, P)}{\dot{m}_{gas} C_{p,gas}} \tag{3.5}$$

where ΔH_R - enthalpy of reaction at current temperature [kJ/kmoleK], χ - fractional conversion of nitrogen, V - catalyst bed volume [m^3], F_{N_2} - molar flow rate at bed inlet, $\dot{m}_i$ - mass flow rate of gas [kg/h].

Due to proprietary reasons authors cannot provide a layout for the heat recovery system in the converter, thus making it impossible to disclose details of the heat recovery model as well. So this part will remain unknown for the reader, however one will not experience any unclarity of the work flow or loose generality of this work.

The model was validated with industrial data of the converter operation. Authors performed a comparison between simulated and measured temperatures (Fig. 3.2) and feed compositions (Table 3.1). One can see a close match between simulated temperature profile within catalyst beds and measured by thermocouples at beds' edges. The error lies with range of few °C. Moreover, prediction of stream composition are also very close to the experimental results. Thus, the model has a good accuracy to be further used for converter simulation and optimization.

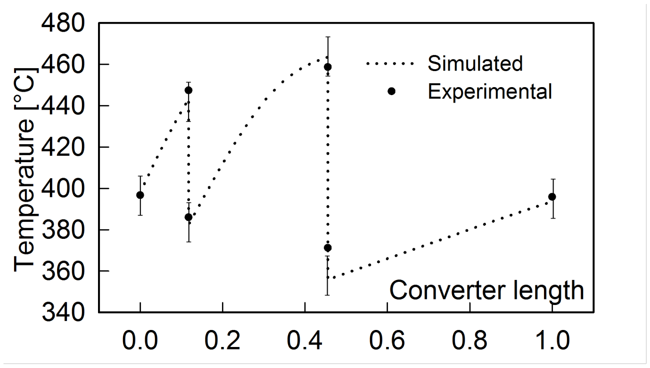

Figure 3.2: Comparison between simulated and observed temperatures along reactor

	Gas stream composition [% mol.]				
	N_2	H_2	NH_3	CH_4	Ar
simulated	23.53	56.38	13.31	5.08	1.70
experimental	23.10	56.50	13.56	5.08	1.71

Table 3.1: Comparison between simulated and experimented gas composition

3.3 Multi-objective optimization of converter operation

The converter's operation is a complex process. It has a number of control and performance parameters which has to be taken in to account in order to operate the unit or perform multi-objective optimization. Proper study of the converter's layout, consultation with process engineers and preliminary model simulations allowed us to narrow down process control parameters for operation to three major: feed gas temperature T_{feed}, quench-to-feed ratio QFR and process pressure P.

The most important industrial criteria of the ammonia converter efficiency is ammonia production. Other objective of engineering importance is the amount of heat recovered within the system. The more heat can recovered the less is needed to provide into the synthesis gas. Firstly, we performed few model simulation to visualize the objective domain for up mentioned process parameters (shown at Fig. 3.3 (a) and (b)). Both objective spaces are convex surfaces with individual maximums located within box-constrained region leading to non-linear optimization problem.

Secondly, the developed model is inconveniently expensive computation-wise taking around 5 minutes of CPU time for a sole simulation. Therefore, an optimization search requiring a large number of model evaluations will result in lengthy runs. So we performed 60 model simulations and used this data to train surrogate models with Eureqa®. A surrogate model was obtained minimizing AIC as goodness-of-fit measure as more robust metrics[38]. As Eureqa® yields a set of models compromising accuracy vs. complexity, we choose one model for each objective which we found to have satisfactory accuracy for MOO.

The obtained models are shown on Fig. 3.3 (c) and (d) for $X_{\mathrm{NH_3}}^{out}$ and HR respectively. One can find some discrepancy between figures *a)* and *c)* in the area of low T_{feed} and QFR, while the other regions show good consistency. However, as it will be shown in Results and Discussion, the obtained optimum lies far from the discrepancy region. Thus, the regression models by Eureqa® can adequately represent original objective functions.

Case 1 : The two objective discussed above were included into two-objective optimization problem. The optimization problem is constrained by maximum bed temperature as it is limited by catalyst manufacturer in order to prevent damaging the catalyst

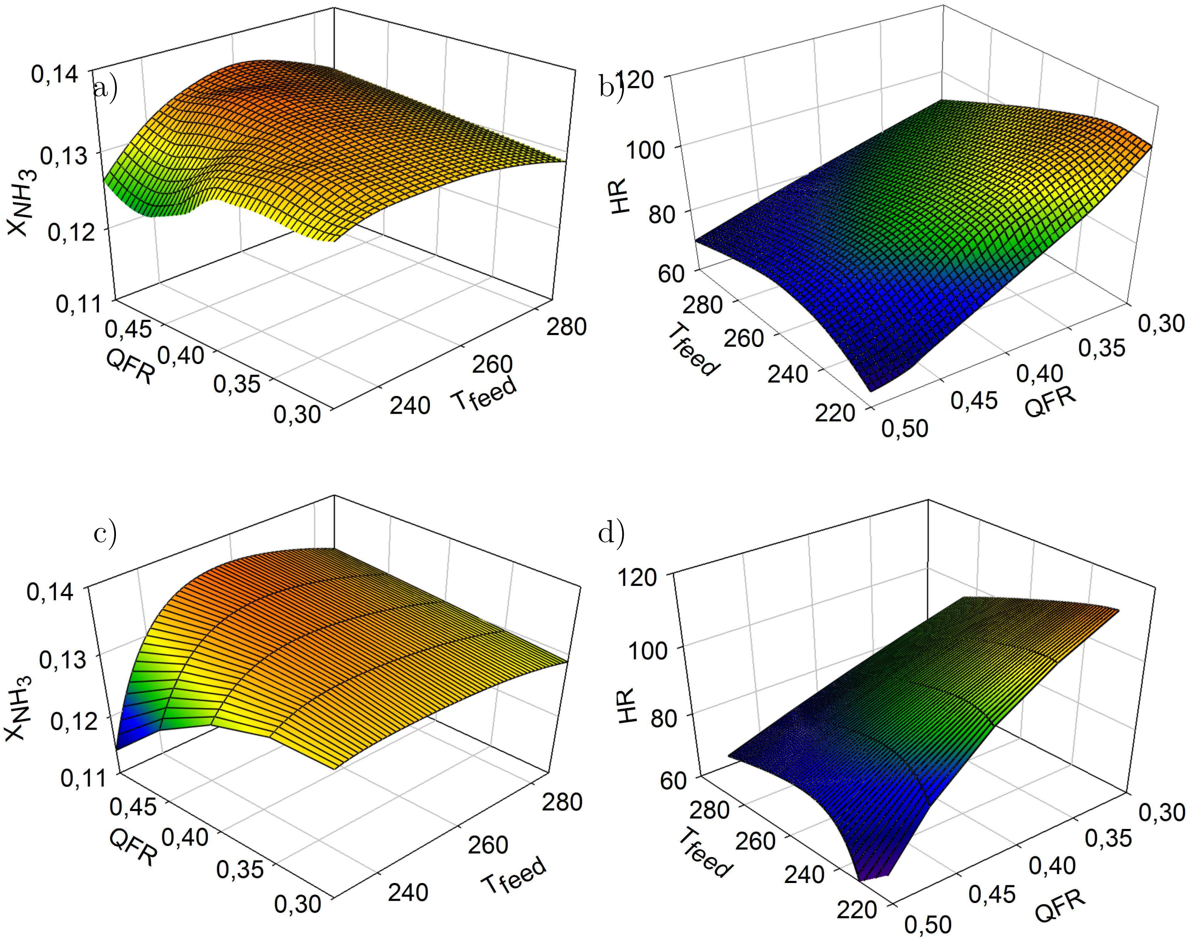

Figure 3.3: Response surfaces for process objectives
Figures a), b) are obtained by simulation of original model, figures c), d) - by surrogate simulation.

Table 3.2: Single objective maximums

Objective	Optimum	Other objective	T_{feed}	Q_{quench}
$X_{\mathrm{NH_3}}^{out}$	0.1354	85.06	249.98	0.45
HR	105.31	0.1310	230.04	0.33

and loss of activity. Industrially feasible domain for process parameters is a subject to minimum and maximum bounds as decided in accordance with industrial practice. The MOO problem is summarized as:

$$maximize \quad I_1(\mathbf{x}) = X_{\mathrm{NH_3}}^{out}$$

$$maximize \quad I_2(\mathbf{x}) = \mathrm{HR}$$

subject to:

$$T_{bed}^{out} \leq T_{max} \quad for \quad each \quad bed$$

$$\mathbf{x} = T_{feed}, Q_{quench}, P \in [min; max]$$

Prior to MOO, corresponding SOO problem was solved with only one objective to be maximized. Individual maximums of the objectives were found with COBYLA method[39](Table 3.2). Firstly, one can find individual maximums of both objectives. Secondly, it is evident that both objectives cannot be satisfied simultaneously. In case of conflicting objectives, the optimal solution should be a Pareto optimal set of points. Therefore, the MOO problem was solved with NSGA-II[24] which allows to treat the problem directly as formulated.

3.4 Multi-objective optimization of converter design

Case 2 : Also, we considered MOO problem involving converter's design parameters. Beside ammonia production, another important process parameters is a total catalyst loading within converter and it distribution among beds. Therefore, another multi-objective optimization problem to to investigate possibility to lower total catalyst volume in reactor while keeping ammonia production high to be solved as follows:

$$maximize \quad I_1(\mathbf{x}) = X_{\mathrm{NH_3}}^{out}$$

$$minimize \quad I_2(\mathbf{x}) = \sum_{i=1}^{3} V_i \quad i = 1 - 3$$

subject to:

$$T_{bed}^{out} \leq T_{max} \quad for \quad each \quad bed$$

$$\mathbf{x} = T_{feed}, Q_{quench}, V_i \in [min; max]$$

3.5 Results and discussion

Case 1. Pareto set of optimal solution for Case 1 was obtained for two different converter pressures. As the converter pressure being the parameter not easily changeable in industry (contrary to feed temperature and quench-to-feed ratio), we solved Case 1 for 85 and 91 atm. independently. Former pressure is found to be most common for the converter, while latter is intended to show the potential changer in converter operation and possible to achieve within the unit. The results are shown in Fig. 3.4. Overall, higher temperatures and QFR favour higher ammonia production. If this is the objective one is striving for, it is necessary to control both parameters simultaneously to stay near optima. However, at higher pressure the impact of quenching is becoming less important thus more attention has to be paid for feed temperature.

One can note that higher pressure is much in favour of higher ammonia production. Any point of 91 atm. set is providing higher molar fraction of ammonia in product. On contrary, lower pressure on average allows for higher heat recovery within converter. Moreover, it also provides a wider range of Pareto optimal solutions for both objectives. If one willing to come from low to high heat recovery (*i.e.* from most right to most left point at 85 atm.), it will allow for 8% in heat saving. Considering large scale of

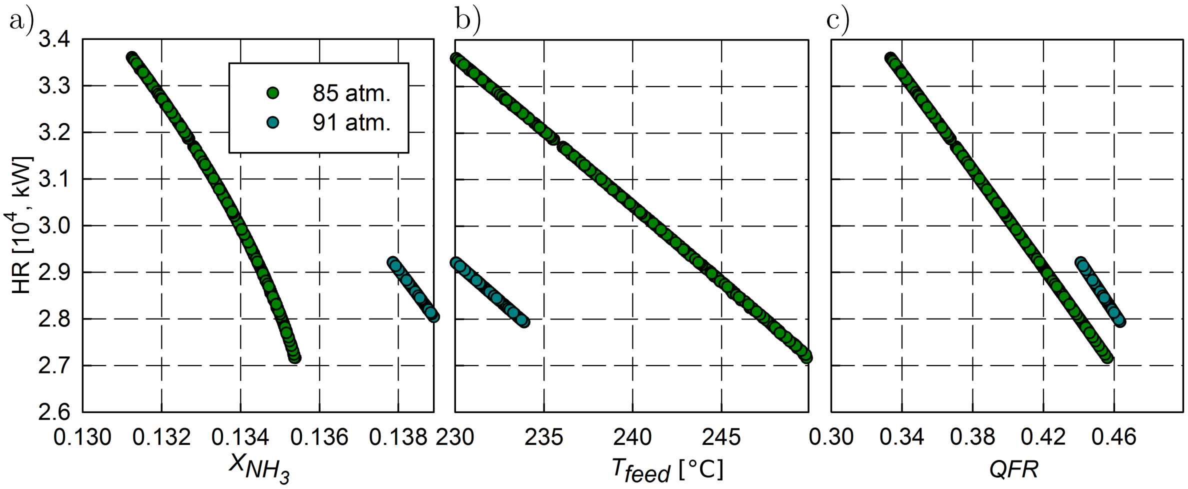

Figure 3.4: Pareto optimal set of solutions for Case 1
Figure a) shows both objectives. Figures b), c) shares the same Y-axis with figure a) and shows relation of process parameters to Pareto-optimal set of objectives.

production it will result in significant heat duty reduction. The range is narrower at higher pressure due to faster reaction rate and heat generation, thus, consequently, more bounded by upper limit on catalyst bed temperature.

If one willing to account for total heat recovery, adding up both ways of heat recoveries - by quenching and through heat recovery systems - the obtained optimal operating conditions are the same. One can see that the most contribution into overall heat recovery is done by means of HR. About 60-70 % is contribution of HR, while remaining part is done through quenching. Thus, main focus in optimization has indeed to be done on efficiency of HR-system rather making it equivalent problem to maximization of total heat recovery.

Case 2. The solution for Case 2 is given at Fig. 3.5. As for Case 1, Fig. 3.5 a) provides a range of objectives. One can find that a range of $X^{out}_{\mathrm{NH}_3}$ is much wider than in case 1 (1.2% vs 0.6%). Also, for every point on the figure ammonia content in the product stream is higher than for any point in Case 1. Therefore, catalyst distribution is another important parameter to consider when designing a converter or loading fresh catalyst at maintenance. As for process parameters, QFR and V_1 hit their upper and lower bound

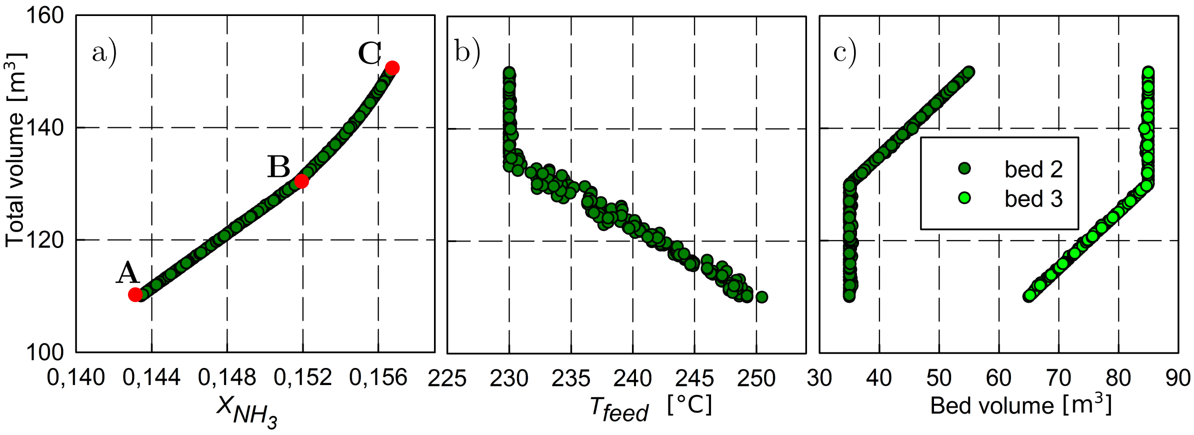

Figure 3.5: Pareto optimal set of solutions for Case 2
Figure a) shows both objectives. Figures b) shares the same Y-axis with figure a) and shows relation of feed temperature to Pareto-optimal set of objectives. QFR is at upper bound, V_1 is at lower bound.

respectively. The relation of other process parameters to Pareto optimal points is given on Fig. 3.5 b) and c). Feed temperature and two other bed volumes are experiencing more complex relations in order to stay Pareto optimal. Firstly, higher total catalyst volume will allow for lower inlet temperature due to higher space times. Secondly, the major decrease in feed temperature (20 °C) and rise in ammonia (0.8 %) is achieved through the increase in third bed catalyst loading. The further boost in ammonia (0.4%) is through increase of the loading in second bed, while keeping T_{feed} and V_3 constant.

To take a closer look into importance of catalyst distribution on converter performance, one can consider three cases from Fig. 3.6 a) highlighted as. A and C correspond to marginal cases with minimum and maximum loading while B depicts solution “in the middle”. In fact, total loading of catalyst at point B is the same as in the converter studied but with different distribution. The existing catalyst distribution is labelled as “original” at Fig. 3.6. Firstly, one can note a major contribution of the first and second beds into overall ammonia production. While first bed loading remains constant, the change in other two can drastically improve ammonia production. Secondly, even lowest catalyst loading provides higher ammonia production by far (“original” vs. A). Needless to say that if one can properly redistribute existing amount of catalyst among beds, it

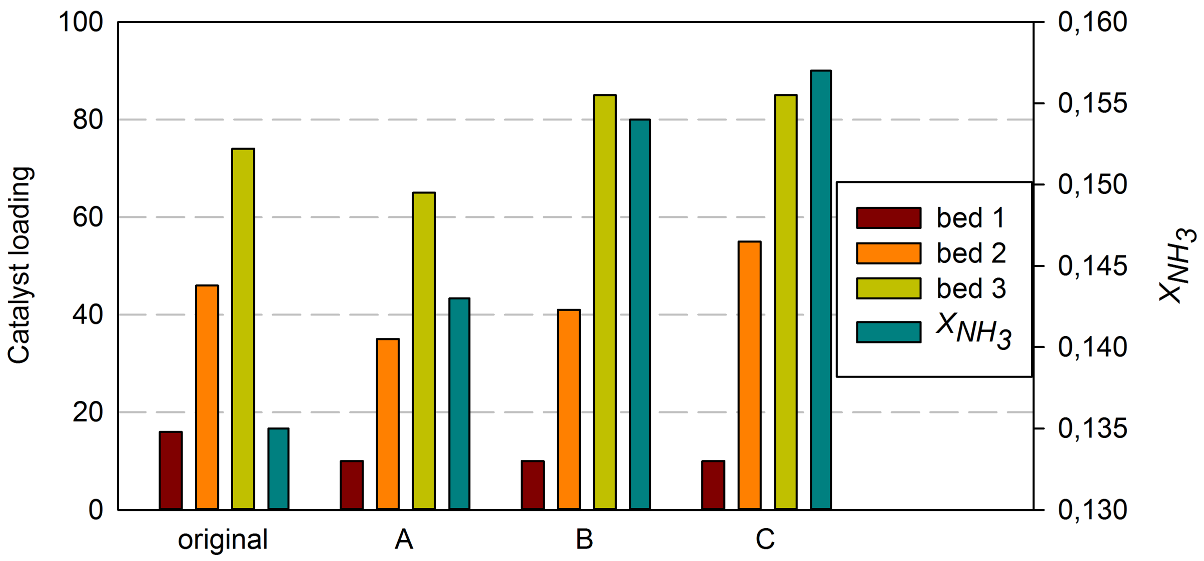

Figure 3.6: Comparison of catalyst loading distributions
Distribution of catalyst among beds at points A, B and C from Fig. 3.5 are compared. "Original" denotes current catalyst distribution in the object of study. Case B in total gives the same amount of catalyst as in "original" case.

can bring even better ammonia production ("original" vs. B).

For all considered cases operating parameters remain in the same range, while pressure is kept at 85 atm. One can recall from optimization of Case 1 that at higher pressure ammonia production increases. Thus, if ammonia production is the first priority, there's even more room for improvement at higher pressures if engineers are willing to increase compression duties and/or if there's no other restrictions to do so.

3.6 Conclusions

A multiobjective study of the industrial ammonia converter was performed. The MOO study was done with use of surrogates trained on simulated data from first-principle model. The surrogate models obtained with Eureqa® have a good accuracy to be used as substitute for original model. Two MOO cases - operation and design optimization - were solved and analyzed with NSGA-II. The most important parameters on the unit operation are found to be feed temperature, quench-to-feed ratio and pressure. Thus, former case yielded a Pareto set of solutions compromising between ammonia production and heat recovery depending on these parameters. The latter case showed that for any point in Pareto set for design MOO ammonia production is higher that in operation MOO. Therefore one can benefit even more with change of total catalyst loading in the converter and/or proper distribution of catalyst among beds. The total ammonia production at any point of Pareto set for design optimization was higher that for operation case even for lower total catalyst loading in converter.

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Chapter 4

Data-Based Modelling And Optimization Of Carbon Dioxide Removal From Process Gas

Nomenclature

$\mathrm{A}-1$	absorption tower
abs	absorbent
$\mathrm{C}-1$	cooler
$\mathrm{D}-1$	desorber
L	liquid level
N_{clust}	number of clusters
n_i	number of points in i^{th} cluster
P	pressure
p	refers to point in cluster
$\mathrm{P}-1$	solvent pump
Q	volumetric flow rate
RMSE	root mean squared error
$\mathrm{S}-1$	separator
SOM	self-organizing maps
T	temperature
X	molar fraction

4.1 Introduction

Carbon dioxide occurs as an undesired flow component in a number of chemical engineering processes, such as industrially mature natural gas treatment ammonia production[1] or power generation, or more modern as biogas production[2], etc. The purpose of CO_2 removal may vary, from gas pre-treatment to its further conversion. Depending on the required extent of carbon dioxide removal, scale of production or other process features there are a number of technologies available nowadays. Carbon dioxide is removed by chemical or physical absorption using selective solvents or solids[3,4], pressure swing adsorption[5]or membrane separation.[6] Some of these ways have long history and wide spread among industries, while others are more modern.

In the large scale processes, the use of physical and chemical solvents is more common. Conventionally, the process undergoes through two stages. Firstly, carbon dioxide capture occurs in a contact unit through direct gas-liquid contact. Later, captured carbon dioxide is released in a solvent-regeneration unit. This absorption-desorption loop allows carbon dioxide removal unit to operate in a continuous mode.

There is significant number of works published in the literature dedicated to the modelling of industrial carbon dioxide removal units. Robinson and Luyben[7] performed a modelling of carbon dioxide removal unit as a part of a large scheme of integrated gasification combined cycle (IGCC). CO_2 along with other contaminants occur there as a result of fuel combustion. They developed a dynamic model using Aspen Dynamics. Optimal equipment design was selected based on desired product purity; and dynamic simulation was performed to evaluate performance of the IGCC plant under disturbing conditions.

Similarly to previous work, Bhattacharyya et al.[8] performed a steady-state simulation of IGCC plant with Aspen Plus. Conceptual way was illustrated in how to optimize IGCC plant, what parameters should be accounted for and how to utilize them while solving optimization problem. However, it was not applied to any existing plant. They used the model for overall three-phase plant optimization while targeting CO_2 capture as one of objective functions. They came up with various scenarios for best plant design decisions.

Kapetaki et al.[9] authors are striving to achieve higher carbon dioxide removal efficiency than the authors of two previous researches. They used Honeywell UniSim for steady state modelling of carbon dioxide removal unit. They investigated two different process operating modes under different operating conditions (e.g. unit pressure, absorbent flow rate) onto process performance (i.e. carbon dioxide capture, power consumption).

Mores et al.[10] performed modelling and optimization study of carbon dioxide removal with monoethanol amine solvent. Their model was implemented with General Algebraic Modeling System. The model underlies complex heat and mass transfer equations with a significant number of process parameters and technological constraints. This work is mainly focused on improvement to be made in solvent regeneration from CO2. To do so two objective functions were proposed: to minimize heat duty in reboiler and to minimize ratio (heat duty in reboiler/CO2 removal).

The object of this study is an industrial solvent-based carbon dioxide absorber. In this work authors intend to utilize different approach for modelling of the latter. Firstly, we are performing the study of real operating unit aimed for synthesis gas purification in the ammonia production chain. Carbon dioxide has to be removed there up to certain percentage in order to avoid catalyst poisoning downstream. While carbon dioxide removal itself on this unit is efficient enough and practically does not raise any optimization problem, but solvent regeneration bears a room for improvement. Therefore, authors are focusing on quality of solvent regeneration. The requirements which constitute quality will be addressed below in process description. Thirdly, we are willing to utilize vast amount of available industrial data. It covers a quite long time span of the unit operating history. This work is done in collaboration with plant engineers, thus their engineering judgment is taken into high consideration. Overall, they are quite satisfied with the mode of the unit operation and quality of treated gas. However, throughout this work we intend to determine most important parameters to be used in process performance improvements having minor interference with the current operation mode. Note: due to proprietary reasons all the data used throughout this paper related to the real operating conditions of the industrial unit is provided in dimensionless form.

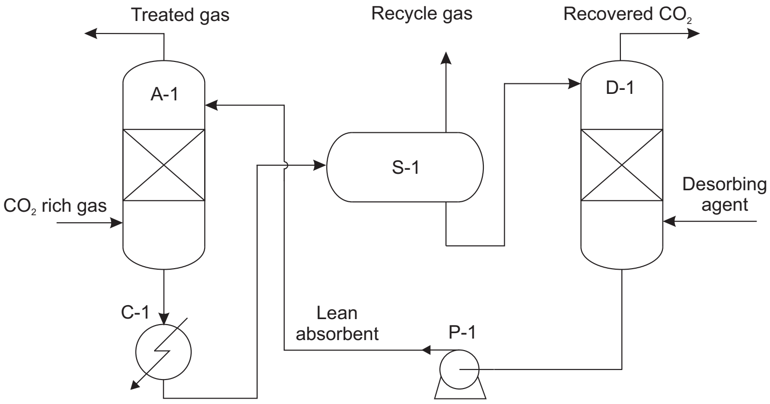

Figure 4.1: Process flow diagram for carbon dioxide removal

4.2 Process description

One of the most conventional technologies for ammonia synthesis uses natural gas as a feedstock. Overall description of ammonia synthesis from natural gas can be found elsewhere.[1] Briefly, the process gas is mainly (80-90 % mol.) made of hydrogen and nitrogen in the ration close to stoichiometric (3:1). The remaining gases are unconverted methane, argon, carbon dioxide and carbon monoxide. Remaining carbon oxides in the gas originate from steam reforming reaction followed by gas shift reaction. A gas stream contains 10-15% mol. of carbon dioxide at the inlet of the treatment unit. If not removed, carbon dioxide will act as a catalyst poison downstream in the ammonia converter.

Thus, carbon dioxide removal unit serves for process gas purification. Untreated gas from shift conversion enters to the bottom of to the packed bed absorber $A-1$ (Fig. 4.1). Lean absorbent is supplied through the top of A-1 where CO_2 removal occurs through gas-liquid absorption in a counter-current fashion. However, absorbent is selective to CO_2, but all of the process gasses are getting captured but in a lesser amount. A second most captured gas is hydrogen. The treated gas leaving from the top of A-1 contains 10-1000 ppm. of carbon dioxide. The actual concentration highly depends on solvent and process operating conditions.

Further, the solvent is freed from captured gases through two stages desorption. Firstly, CO_2-rich solvent leaves from the bottom of $A - 1$ to the cooler $C - 1$ where its temperature drops down. When cooled, it flows into separator $S - 1$. Prior to entering $S - 1$ flow pressure is dropped and absorbed gases are partially released from top (Recycle gas). Recycle gas is mainly carbon dioxide and hydrogen with minor part of other gases from the gas stream. Then, half-rich CO_2 solvent flows to the desorber $D - 1$. Similarly to $A - 1$, the desorber $D - 1$ is a packed bed contact unit there remaining gases are stripped away fully regenerating lean solvent. Remaining gases are stripped from the top of a column. Lean absorbent is compressed in the pump $P - 1$ up to operating pressure and recycled back to the absorber.

4.3 Process modelling

The instrumentation and chromatography analysis data obtained from industrial carbon dioxide recovery unit was used for the modelling. The data covers a time span for several years of the unit operation. It includes process instrumentation readings such as from pressure or temperature indicators, flow meters, etc., as well as chromatography analysis of gas flows at the unit. The entire set of original data was pre-treated to remove irrelevant information which could occur due to indicators failure and malfunction, a human error or errors of any kind.

Firstly, data inspection was done visually appealing to common sense and engineering judgment of the authors and plant engineers. Then, it was clustered using self-organizing maps (SOM) (described below) in order to determine outlying groups of data. After prescreening was accomplished, the post-treated data set contained around 350 points.

Operating range of real industrial unit is quite narrow, *i.e.* process parameters cannot vary in wide range due to some engineering restrictions. Hence, the correlations between inputs and outputs can assumed to be linear, therefore linear regression to be used.

As with majority of data-based models, during training one may face over-fitting problem. To resolve the faced problem with models training, one may take a closer look into the operation of a large scale industrial unit and, particularly, the instrumentation readings. The carbon dioxide removal unit is a continuously operating unit serving for the only purpose to provide treated gas of a certain quality for its further downstream conversion. This quality has to be maintained all the time for stable plant operation. As with many large scale continuous units, the object of this study is operating in the steady state most of the time. It is worth to admit that in reality the instrumentation readings and analysis during a steady state operation are obviously not constant, they are subject to random noise, fluctuations in feedstock quality and feed rate, malfunctioning, etc. Transition between the states occurs when engineers decide to change operating conditions and shift unit into a new state.

At the same time, the instrumentation readings and gas analysis occur on the regular basis and are almost evenly distributed in time. Thus, the longer the unit was in *state a* the more data points are retrieved from the system. When the unit changed its state into *state b* for a shorter time, we end up with fewer points for the new state. However, this points deliver for us useful information about units performance. This is happening several times during the entire unit operation (*state c*, etc.). Lets consider a generic uni-variate case of such unit operation (Fig. 4.2).

Imagine we have three real states a unit have been into over observed period of time. They are marked in solid black circles. If we were able to measure these values, applying least square method we would get an ideal regression model (black line). No doubt it is impossible to achieve it with real data because all the measurements are subject of noise and uncertainty.

Lets compare two independent cases. In the *case 1* measurements are done rarely, so we have just a few points representing each true state (green dots). In the case 2, measurements were more frequent and more observation points were gathered (red dots).

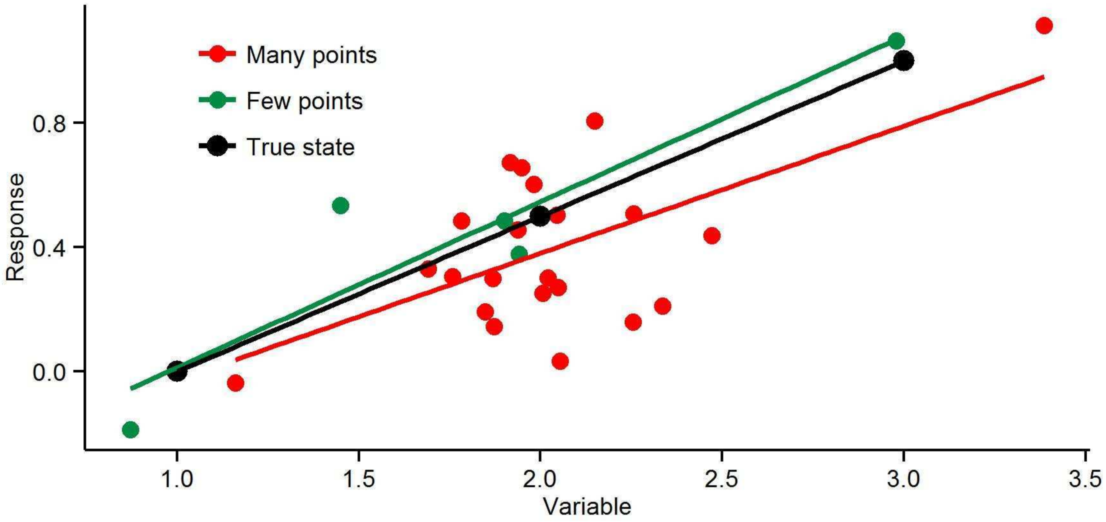

Figure 4.2: Single variable generic case for linear regression of industrial data

Since time spans of true states are differ time, we have more points representing state 2 and less for states 1 and 3. If we apply least square regression to both cases, we can conclude that if we have bigger data cloud for state 2 (i.e. case 2), it causes more significant deviation from ideal case than having less points (i.e. case 1). So we obtain distortion of results if we dont account for that. Thus, it is necessary to diminish impact of data clouds onto regression model.

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If we take a closer look onto industrial data, we can find that there are some denser regions, while some other are scattered or even few points at all (Fig. 4.3). Lets do not forget that real problem is multivariate and similar effects can be observed in other dimensions. If we disregard this phenomena we obtain regression model which tends to deviate more from real units performance. Authors understand that perception of

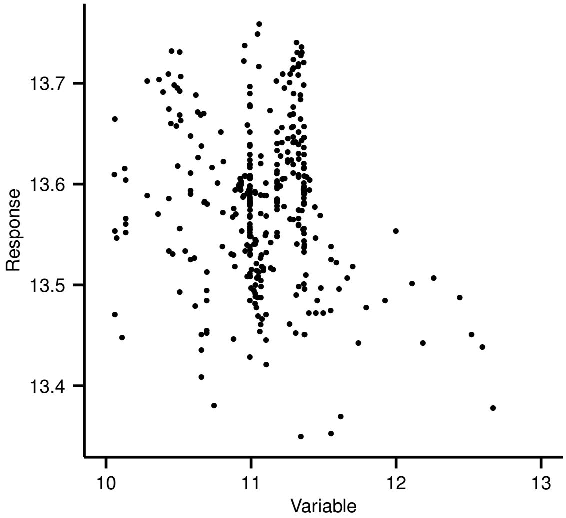

Figure 4.3: Example of real industrial data

whether the model underestimates or overestimates the real performance is unclear and subjective. Thus, the criteria to decide about models ability to describe units performance was based on common sense and long-time experience of plant engineers who were able to provide us with a reliable feedback on model performance.

To diminish impact of dense regions we are going to incorporate least square regression with clustering algorithm. Clustering will allow for aggregation points within dense regions and diminish effect of large clusters. To clarify, by this means we do not intend to explicitly divide data into the exact number of steady states in which unit has been operated. We just willing to account for the impact of big data clouds, thus mitigating their distortion effect and cutting through the clusters.

4.4 About clustering

Clustering is a general word to describe a number of methods aimed for grouping data. The criteria for grouping as well as techniques vary widely.[11] For the sake of clarity, one can say that points within a particular cluster bear more resemblance to each other than to points belonging to another cluster. For example, similarity between data points can be expressed as metric distance, e.g. Euclidean distance in K-means clustering[12] or some other cases of Minkowski distance is used in hierarchical clustering[13].

In the purpose of this work, authors used a self-organizing maps also known as Kohonen maps (SOM).[14] SOMs provide mapping of multi-dimensional variables into two-dimensional space. One pre-defines SOM topology first (*i.e.* type of grid). Each node in the grid is referred as a codebook vector. Then SOM learning algorithm maps original data into discrete locations around codebooks. Thus to be said that each codebook vector is representation of group of data points (cluster) gathered around it. The entire set of them in the SOM grid depicts structure of entire data set. More detailed description of learning algorithm can be found elsewhere.[14,15]

Fig. 4.4 shows the example of codebook vectors obtained with SOM while clustering industrial data. Values of data points within each cluster are in the close proximity with values of codebook vectors. Coloured leaves with each sub diagram illustrate relative values of each process parameter. For example, counting row-wise from top left corner, one can say cluster three has larger values of $Q_{\mathrm{A-1}}$ and $X_{\mathrm{H_2}}^{\mathrm{A-1}}$ or cluster seven has higher values of Q_{abs} than others, etc. Thus, SOM mapping provides one, firstly, with intuitive sense of the data structure. It is worth to note that from a practical point of view it a convenient way for outlier screening in the raw data. One can cluster data first and then check out clusters with outstanding values. Secondly, SOM mapping provides one directly with clusters of data assigning each point to a particular coding vector.

4.5 Model training and validation

The following assumptions have been made prior to the modelling. Firstly, absorber $\mathrm{A}-1$ operates in steady state under the same conditions, *i.e.* feedstock flow conditions and unit operating conditions are constant. Thus, flows leaving $\mathrm{A}-1$ from top and

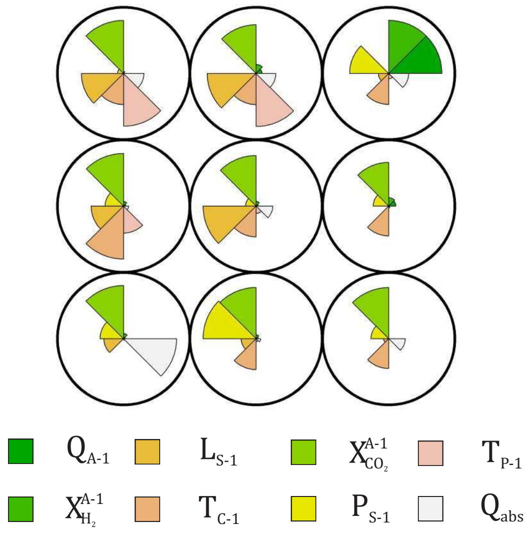

Figure 4.4: SOM coding vectors

bottom are also have constant conditions, *i.e.* composition, temperature, pressure, etc. We find it a reasonable assumption, because the plant operates at constant production rate and it is crucial to maintain the quality of treated gas over time to provide stable operation of ammonia synthesis reactor. As it was confirmed by distribution of operating conditions over considered time span.

Secondly, we assume a feed rate of stripping agent constant since no flow meter is installed on the line to retrieve this data. Thirdly, as we mainly interested in two most absorbed components CO_2 and H_2 we dont consider remaining components separately, but as lump of. Summarizing, to perform modelling and evaluate performance of carbon dioxide removal unit authors selected to predict 3 response properties (Table 4.1) based on the defined set of variables. Any other needed flow properties within the unit can be calculated from mass balance of the process.

Original data set was divided into training and validation sets. The former was used for model fitting and the latter for evaluating model performance. The training procedure was as follows. The training data was clustered into N_{clust} clusters with each

Table 4.1: Performance criteria of carbon dioxide removal unit used in the modelling

Response	Description
$Q_{\mathrm{S-1}}^{top}$	Volumetric feed rate of recycle gases from $\mathrm{S-1}$
$X_{\mathrm{CO_2}}^{\mathrm{D-1}}$	Mole fraction of $\mathrm{CO_2}$ in top gas from $\mathrm{D-1}$
$X_{\mathrm{H_2}}^{\mathrm{D-1}}$	Mole fraction of $\mathrm{H_2}$ in top gas from $\mathrm{D-1}$

Table 4.2: Performance criteria of carbon dioxide removal unit used in the modelling

Variable	Description
$L_{\mathrm{S-1}}$	Liquid level in separator $\mathrm{S-1}$
$P_{\mathrm{A-1}}$	Pressure in absorber $\mathrm{A-1}$
$P_{\mathrm{D-1}}$	Pressure in desorber $\mathrm{D-1}$
$P_{\mathrm{S-1}}$	Pressure in separator $\mathrm{S-1}$
$T_{\mathrm{C-1}}$	Temperature of $\mathrm{CO_2}$ reach absorbent after cooler $\mathrm{C-1}$
$T_{\mathrm{P-1}}$	Temperature of lean absorbent after pump $\mathrm{P-1}$
$Q_{\mathrm{A-1}}^{in}$	Volumetric feed rate of gas into absorber $\mathrm{A-1}$
Q_{abs}	Volumetric feed rate of absorbent in $\mathrm{CO_2}$ removal loop
$X_{\mathrm{CO_2}}^{\mathrm{A-1}}$	Mole fraction of $\mathrm{CO_2}$ in feed gas to $\mathrm{A-1}$
$X_{\mathrm{H_2}}^{\mathrm{A-1}}$	Mole fraction of $\mathrm{h_2}$ in feed gas to $\mathrm{A-1}$

cluster having n_i points. Point p_i^j is given weight of $1/n_i$. Thus points within bigger clusters are assigned smaller individual weights and clusters have even impact on the regression. Then least square linear regression model is fitted over weighted data, and models performance is evaluated with validation data. For validation score root mean squared error (RMSE) is used. The procedure is repeated for different N_{clust} and the one with least RMSE score is chosen.

4.6 Variable selection and ranking

Prior to modelling, one needs to be explained with procedure of variable selection for modelling. We selected all process parameters which are *a)* aimed for control of process performance, *b)* parameters which affect process performance thermodynamic-wise and *c)* which are stored in the industrial data base in a sufficient amount. List of selected variables is given in Table 4.2.

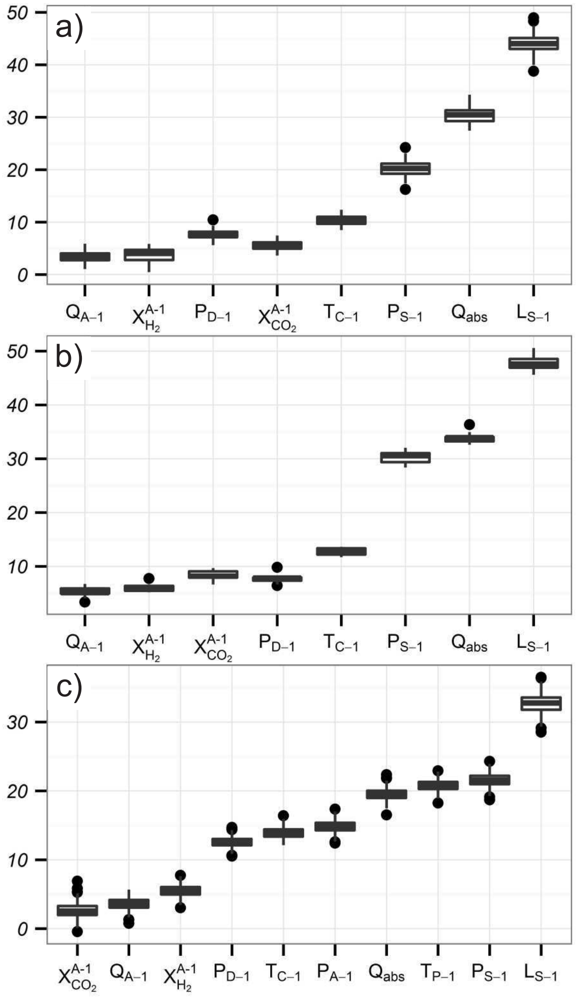

Figure 4.5: Variable importance test with Boruta: a) $X^{\mathrm{D-1}}_{\mathrm{H_2}}$, b) $X^{\mathrm{D-1}}_{\mathrm{CO_2}}$, c) $Q^{top}_{\mathrm{S-1}}$

Then variables were tested and ranked for relative importance onto each of the response parameters. Boruta method[16] was used for feature selection. The method ranks variables based on the Z-score of Random Forest.[17] In addition, it creates a number of random attributes and compares their Z-cores with scores ones of real attributes. Real attributes only with Z-scores higher than maximum the Z-core of random attributes are considered as relevant for prediction of the response. Fig. 4.5(a-c) shows the ranking of accepted variable for each of three responses.

4.7 Results and discussion

Carbon dioxide unit model is developed in R language.[18] Additional R packages caret[19], [20] are used for data pre-processing and clustering respectively, package Boruta[21] is used for variable ranking.

4.8 Model validation

Self-organizing maps of rectangular topology are used for clustering, since they have shown good performance in clustering industrial data on the data pre-processing stage. However, authors believe that the use of other clustering methods will not change the approach significantly.

Firstly, one can conclude from Fig. 4.6 that fewer number of clusters allows for RMSE reduction better than more clusters. Maximum SOM topology 6 by 6 SOM was chosen since mapping 350 points into larger number of clusters is not reasonable.

Secondly, one can admit that in some cases the proposed method works better than in others. Thus, in case of $X^{\mathrm{D-1}}_{\mathrm{CO_2}}$ and $Q^{top}_{\mathrm{S-1}}$ and $X^{\mathrm{D-1}}_{\mathrm{H_2}}$ (Fig. 4.6a,c) we obtain evident solution for the SOM size depending on RMSE values. In case $X^{\mathrm{D-1}}_{\mathrm{CO_2}}$ it was not clear which SOM topology to choose, thus for consistency with two other cases we selected 3 by 3. Table 3 shows RMSE obtained on validation data set. Fig. 4.7 depicts validation plots for property prediction.

On the next step, we attempted to reduce a number of variables used for regression. Since not all of them are possible to include into optimization problem due to technological constraints, we intend to limit their number only to the most industrially important ones. We took Z-score of Boruta test as a measure of relative importance and fitted the model removing less important variables one by one (*i.e.* from left to right on Fig. 4.5. Fig. 4.8 shows the effect of number of variables on RMSE. It is observed that by use of

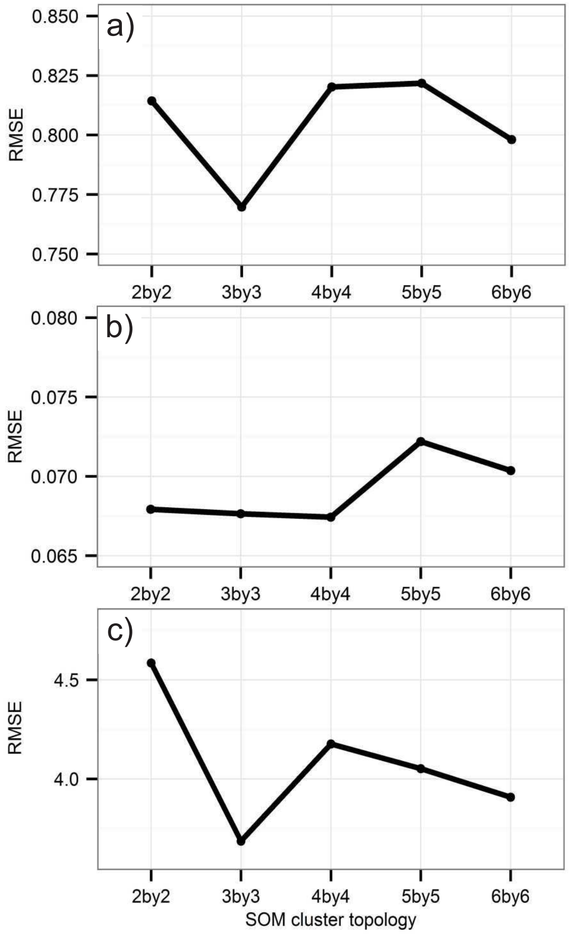

Figure 4.6: Cluster size vs. RMSE: a) $X^{\mathrm{D-1}}_{\mathrm{H_2}}$, b) $X^{\mathrm{D-1}}_{\mathrm{CO_2}}$, c) $Q^{top}_{\mathrm{S-1}}$

less number of variables (comparing to the original ones, *i.e.* number of removed variables = 0) it is possible to further reduce cross validation error.

While selecting the finalized number of variables for regression, authors compromised between the minimum RMSE score and practical importance of the variables. The finalized variables are given in Table 4.3.

Here it is worth to notice one fact about chosen process variables. Liquid level in separator $L_{\mathrm{S-1}}$ has the highest Z-score among other variables for all responses, thus having significant effect towards process performance. Industrially-wise, it is relatively simple to control liquid level in the vessel rather any other parameters, such as temperature or pressure. The variations in the latter might be restricted due to design, safety or

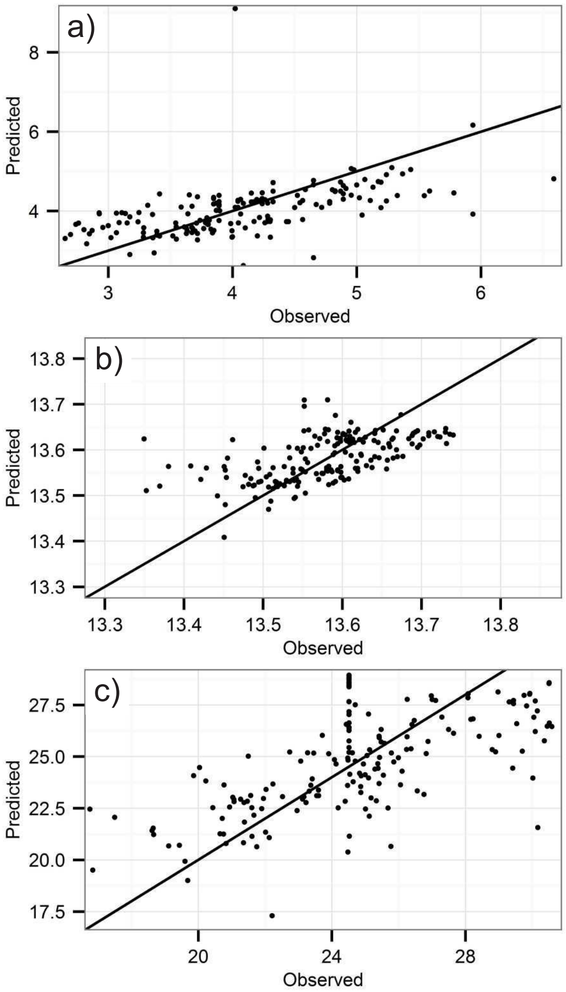

Figure 4.7: Validation plot: a) $X_{\mathrm{H_2}}^{\mathrm{D-1}}$, b) $X_{\mathrm{CO_2}}^{\mathrm{D-1}}$, c) $Q_{\mathrm{S-1}}^{top}$

other engineering reasons. Should we apply conventional first principle modelling for carbon dioxide removal in the unit, it would be problematic to account for that process parameter as a decision variable for modelling and optimization. Authors believe that this phenomenon might happen due to change in the residence time of absorbent in the vessel. The hypothesis makes sense, since higher residents time favour separation of absorbed gases. However, the exact reason for this fact has to be established in the further research, which might involve CFD modelling and simulation.

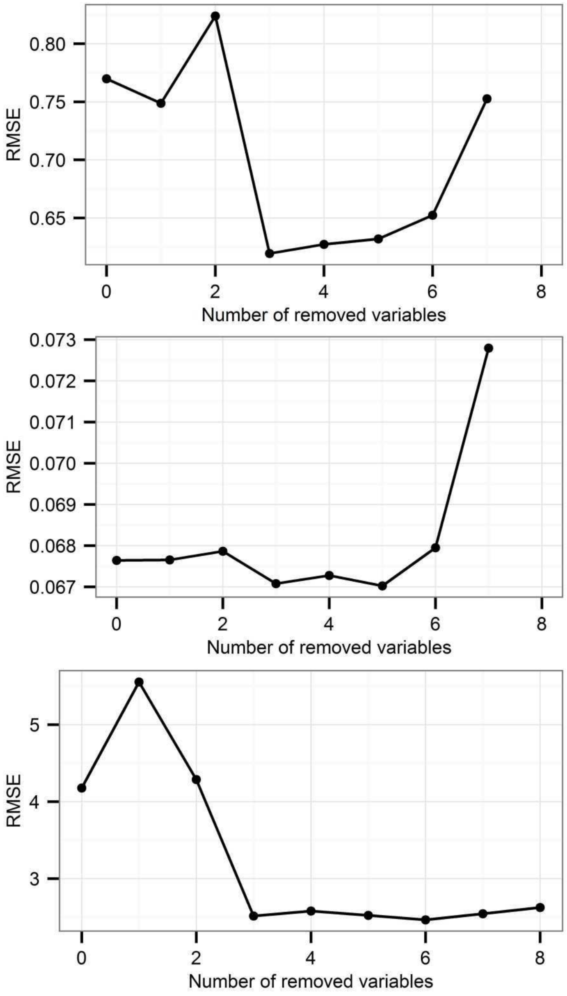

Figure 4.8: Effect of number of variables on RMSE: a) $X_{\mathrm{H_2}}^{\mathrm{D-1}}$, b) $X_{\mathrm{CO_2}}^{\mathrm{D-1}}$, c) $Q_{\mathrm{S-1}}^{top}$

4.9 Operation optimization

Out of 5 process parameters used for modelling (Table), two were selected to be used as decision variables (Q_{abs} and $L_{\mathrm{S-1}}$), while others are keep constant at their industrially feasible values. Values of $T_{\mathrm{C-1}}$ and $P_{\mathrm{S-1}}$ are taken at the designed values. $T_{\mathrm{P-1}}$ cannot be controlled directly, thus the average value for the observed period of time is taken. Upper and lower bounds for Q_{abs} and $L_{\mathrm{S-1}}$ are chosen in accordance with industrial values.

Objectives for optimization were established as *1)* to achieve carbon dioxide flow from

Table 4.3: Performance criteria of carbon dioxide removal unit used in the modelling

Response	Number of removed variables	Variables	RMSE
$X_{\mathrm{H_2}}^{\mathrm{D-1}}$	4	$T_{\mathrm{C-1}}$ $P_{\mathrm{S-1}}$ Q_{abs} $L_{\mathrm{S-1}}$	0.6200
$X_{\mathrm{CO_2}}^{\mathrm{D-1}}$	4	$T_{\mathrm{C-1}}$ $P_{\mathrm{S-1}}$ Q_{abs} $L_{\mathrm{S-1}}$	0.0673
$Q_{\mathrm{S-1}}^{top}$	4	Q_{abs} $T_{\mathrm{P-1}}$ $P_{\mathrm{S-1}}$ $L_{\mathrm{S-1}}$	2.4635

desorber $\mathrm{D}-1$ of a given purity and *2)* to recover more hydrogen from $\mathrm{S}-1$. One can summarize optimization problem as follows:

$$\begin{gathered} I_1 : X_{\mathrm{CO_2}}^{\mathrm{D-1}} = X_{\mathrm{CO_2}}^{target} I_2 : \mathrm{maximize} Q_{\mathrm{h_2}}^{\mathrm{S-1}} \\ \mathrm{subject} \quad \mathrm{to:} \\ \min \leq Q_{abs}, L_{\mathrm{S-1}} \leq \max \\ T_{\mathrm{C-1}}, P_{\mathrm{S-1}}, T_{\mathrm{P-1}} = \mathrm{constant} \end{gathered} \tag{4.1}$$

Fig. 4.9 depicts the response surface between decision variables and either of objectives. Firstly, one can note that two objectives are not in conflict. Either of decision parameters favouring one of objectives favours another one as well. Industrial-wise, it is an advantageous phenomenon. It is possible to satisfy both objective at the same time, thus avoiding any compromising solution. Thus it is needed to increase the liquid level $L_{\mathrm{S-1}}$ in $\mathrm{S}-1$ and lower absorbent circulation rate in the system to improve gas recovery.

Secondly, there is a vast possibility for process performance improvement. The yellow line shows the current operating values for $X_{\mathrm{CO_2}}^{\mathrm{D-1}}$ and $Q_{\mathrm{H_2}}^{\mathrm{S-1}}$. One the one hand, it is possible to reach the goal of I_1, because the point lies within the plane. However, at that

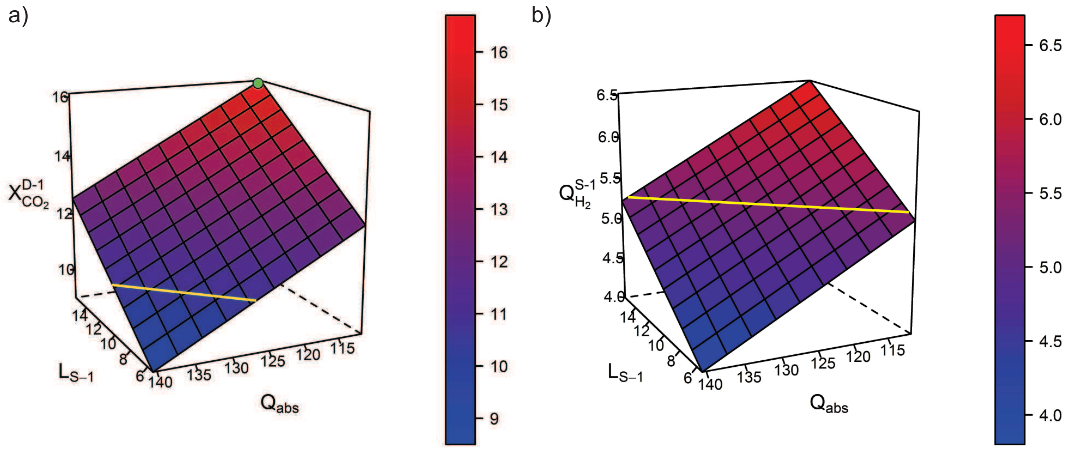

Figure 4.9: Process parameters vs. objectives. a) $X^{\mathrm{D-1}}_{\mathrm{CO_2}}$, b) $Q^{top}_{\mathrm{S-1}}$
Yellow lines are representing intersection of current operation plane with the response surface.
Green dot indicates the goal value for $X^{\mathrm{D-1}}_{\mathrm{CO_2}}$

point decision variables both hit its bounds ($L_{\mathrm{S-1}}$ reach upper while Q_{abs} reach lower). Even though it is not always possible to completely minimize absorbent circulation rate (e.g. due to unexpected overflow of synthesis gas to $\mathrm{A-1}$), but the unit still has capacity to operate with improved performance. Operation-wise, it is relatively easy to change liquid level in the vessel with regard to other process conditions. Increase in the level alone provides significant performance boost even when $Q^{\mathrm{S-1}}_{\mathrm{H_2}}$ is not at the minimum.

4.10 Conclusions

In this work data-based modelling approach is utilized in order to optimize the recovery of valuable gases of carbon dioxide removal unit. Carbon dioxide removal technology information, process flow diagram and description as well as data for several years of plant operation are used for modelling. Linear relations between process and performance parameters are assumed due to narrow operation range and engineering limitations. Data-based model was built as conjunction of self-organizing maps with least square linear model. Model validation was done with industrial data. It has achieved satisfactory performance in order to solve the proposed optimization task. The number of relevant process parameters were narrowed down with Boruta algorithm (i.e. liquid level in separator and absorbent circulation rate). The model revealed significant room for process performance improvements. It is possible to reach the goal of optimization task within the process bounds.

Nomenclature

A − 1	absorption tower
abs	absorbent
C − 1	cooler
D − 1	desorber
L	liquid level
N_{clust}	number of clusters
n_i	number of points in i^{th} cluster
P	pressure
p	refers to point in cluster
P − 1	solvent pump
Q	volumetric flow rate
RMSE	root mean squared error
S − 1	separator
SOM	self-organizing maps
T	temperature
X	molar fraction

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Chapter 5

Multi-objective optimization of the industrial ammonia converter with respect to catalyst deactivation

5.1 Introduction

Ammonia synthesis has a major importance for chemical industry. It has been one of the first processes commercialized at industrial scale. Ammonia has been used widely in different areas - from direct application and manufacturing of agricultural fertilizers (e.g. urea, ammonium nitrate) to production of polymer fibers and explosives.[1]

The way to improve performance of ammonia synthesis in the existing units is process simulation using comprehensive mathematical models followed by numerical optimization. Having a valid model is essential for accurate representation of an industrial system. The subject has been continuously drawing attention over the years as a number of works are present in the literature. Models have been developed for converters of different designs, *e.g.* for autothermal converters[2–4], with multiple adiabatic catalyst beds[5–7]. Models differ in their complexity, from simple plug flow to more comprehensive heterogeneous ones accounting for species transport in catalyst pores. Application of heterogeneous models to industrial converter modelling showed a very good consistency with industrial data and to be more robust.[6,8]

Also, attempts have been made towards optimization of converter performance. Most of works have maximization of ammonia production as the main objective[6,9], while other maximize overall economic return of the process.[4,10] However, none of the works to the best of authors knowledge, use multi-objective approach for converter optimization (MOO). As the industrial ammonia converter being a complex system, it is beneficial to include more than one objective into consideration. MOO has been successfully applied for a number of industrial processes. Many works have been reported for MOO of oil refining processes[11–16], polymer manufacturing[17–22], hydrogen plants[23–26], and many others. Therefore, there's no doubt that applying MOO is beneficial and able to provide better operating conditions for ammonia converter.

Another side of converter optimization that has not been addressed is account for catalyst deactivation. It is the case with many solid catalysts that their performance drops with time.[27] Therefore, it is important to optimize converter performance with respect to changing activity of catalyst.[28] Ammonia catalyst deactivation can be happening due to absorption of oxygen compounds (*i.e.* CO, CO_2, H_2O) and non-metallic compounds(*i.e.* sulphur or arsenic) if any present in the process gas stream. However, absorption of poisonous compounds on catalyst surface is reversible, but poisoning is stable and activity does not return to it original state.[29] Even though short-term operation-wise catalyst deactivation is not the most crucial issue as catalyst lifetime is quite long (reaching up to several years[1]), but in a long run optimal operating conditions are still different. Therefore, it is necessary to adjust them with respect to catalyst deactivation at real process conditions.

In this work, we perform multi-objective optimization study of industrial ammonia converter. We use first principle mathematical model of catalytic converter. It accounts for heterogeneous gas-solid reaction over catalyst and utilizes model for heat recovery system used in the object of study. The model was used to estimate catalyst deactivation rate and kinetic parameters of catalyst at different lifetimes. In order to do estimation, we propose a method to treat industrial data and extract valuable information from it. Finally, the MOO of converter performance was done with respect to catalyst deactivation.

5.2 Overview of converter model

In the Haber process ammonia is produced through the reaction of hydrogen and nitrogen (Eq. 5.1). The reaction is carried out under elevated temperature and pressure to suffice significant yield. The Eq. 5.1 is a gas-solid reaction occurring in presence of iron or ruthenium catalyst. The catalytic ammonia converter is made of few packed beds. The reaction mixture is sequentially fed into beds to produced ammonia in a number of

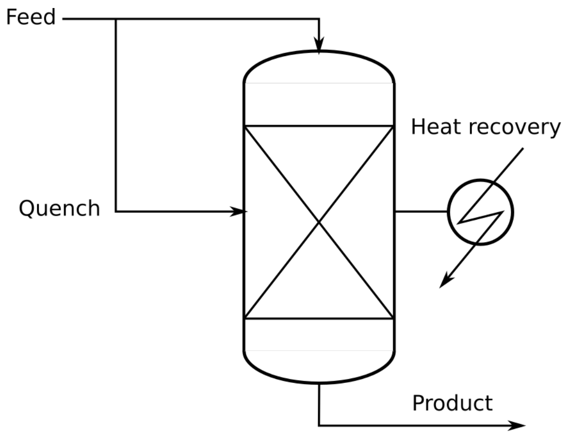


Figure 5.1: Ammonia converter schematic

steps. The intermediate cooling is essential as the reaction 5.1 is exothermic. To prevent catalyst from exposure to high temperatures and shift reaction equilibrium the excess heat is removed between beds.

The object of study is a three bed ammonia converter. The simplified layout is provided at Fig. 5.1. The synthesis gas is split into two flows - for main feed and quench. The main feed enters prior the first bed, while quenching is done in between. The process gas passes through a bed and experiences a temperature rise. This is where quenching and heat recovery is used - to remove the excess heat from the gas stream.

The model mainly consist of four parts covering phenomena occurring during ammonia synthesis. They are reaction kinetic, intraparticle species diffusion, catalyst bed hydrodynamics and model of heat recovery system. The detailed description can be found below.

Note. This work was done on existing ammonia converter and real industrial data was used. Due to proprietary reasons authors cannot disclose full layout of converter and model details. Therefore, heat transfer system and catalyst bed arrangement will remain unknown for the reader. Also, all numbers related to process operating conditions are given in dimensionless form. However, reader will not loose generality of the work flow as we are mainly focusing on process optimization and relative trends in variables.

5.2.1 Reaction kinetics

Ammonia synthesis is done according to the reaction:

$$N_2 + 3\,H_2 \longleftrightarrow 2\,NH_3, \quad \Delta H^0_{298} = -46.22 \quad \text{kJ/mol} \tag{5.1}$$

Ammonia synthesis is a mature process and extends back over decades, but there's still no single opinion about reaction mechanism on the surface of catalyst. So, a number of them are proposed in the literature along with different kinetic expressions.[30–34] The Temkin equation (Eq.5.2) is found to be most accurate and applicable, therefore used for the model:

$$R_{NH_3} = k_2\left[K_a^2 f_{N_2}\left(\frac{f_{H2}^3}{f_{NH_3}^2}\right)^{\alpha} - \left(\frac{f_{NH_3}^2}{f_{H_2}^3}\right)^{1-\alpha}\right] \tag{5.2}$$

The expression for equilibrium constant K_a is taken from Gillespie and Beattie[35] (Eq. 5.3):

$$logK_a = -2.691122logT - 5.519265\times10^{-5}T + 1.848863\times10^{-7}T^2 + 2001.6/T + 2.6899 \tag{5.3}$$

Fugacity of i^{th} component found as:

$$f_i = \phi_i X_i P \tag{5.4}$$

5.2.2 Intraparticle dissuion

Governing mass balance equation used as in Elnashaie et al.[8]. The Eq. 5.5 assumes Fick diffusion of species with catalyst pores:

$$\frac{d^2X_i}{d\omega^2} - \left(\frac{2}{\nu_i + 2X_i}\right)\left(\frac{dX_i}{d\omega}\right)^2 + \frac{2}{\omega}\frac{dX_i}{d\omega} = -\left[\frac{R_p^2}{CD_{ie}}\left(\nu_i + 2X_i\right)\right]\frac{R_{NH_3}(X,T,P)}{1-\epsilon} \tag{5.5}$$

subject to boundary conditions:

$$\omega = 0: \quad \frac{dX_i}{d\omega} = 0$$

$$\omega = 1: \quad X_i = X_i(bulk)$$

Solving the following equation one can find concentration profile in radial direction of catalyst particle and then incorporate it as effectiveness factor η:

$$\eta = \frac{\int_0^1 \omega^2 R_{NH_3}(\omega, X, T, P)d\omega}{R_{NH_{3bulk}}(X_{bulk}, T_{bulk}, P_{bulk})} \tag{5.6}$$

5.2.3 Mass and energy balance

For catalyst bed hydrodynamics model we adopt one-dimensional plug flow model. Therefore, differential mass and energy balance equations are written as:

$$\begin{cases} \dfrac{d\chi}{dV} = \dfrac{\eta R_{NH_3}(\mathbf{X}, T, P)}{2F^0_{N_2}} \\ \dfrac{dT}{dV} = \dfrac{(-\Delta H_R)\eta R_{NH_3}(\mathbf{X}, T, P)}{\dot{m}_{gas} C_{p,gas}} \end{cases} \tag{5.7}$$

5.3 Industrial data analysis

Industrial process control has been broadly upgraded over last decades. It has turned digital with all the sensors connected into a sole database. This allows for continuous monitoring of the system and non-stop gathering of process history. With hundreds of sensors serving a single unit and sending readings a number times per second, this fact made large arrays of data for researchers and engineers to analyze and benefit from.

Ammonia synthesis is a continuous large scale process. As with majority of industrial units, most of the time on line operation is in (pseudo) steady state, *i.e.* control and performance parameters are time-independent. But considering long time run, these process parameters do no remain constant entire time. Usually, the unit changes its steady states through operation. Quite often, transition from one steady state to another is controlled by process operators. When needed, they change one or more process control parameters thus affecting the performance. For example, this might be necessary when feed stock is changed in terms of quality or rate, some auxiliary equipment experienced failure and immediate reaction is needed, etc. The list of reasons is limitless due to different complexity of processes.

The time needed for transition from one steady state to another is usually quite smaller than the time unit spends in either of steady states. Therefore, the majority of instrumental reading will be reflecting the steady states of unit operation rather then transition information. Also, those reading do not genuinely depict true states due to short term fluctuations of process parameters, sensor noise, failures and misreading. Thus, any data entry at time t is an approximation of corresponding unit state. More important, a data entry might be a bad approximation if signal at the moment was subject to large deviation for any up mentioned reason. And not least important, since data arrays are large and sometimes cover time span of few years, it is impossible to genuinely recover time points when did steady state transitions happen. Quite often other non-numeric details of unit operation are lost, since process operators and engineers are rotating, forget things, thus unable to provide all auxiliary information. Thus the one willing to analyze this data is faced with problem of approximation of steady state history and recovery of information from raw data. The specific features of data is as follows:

- Data is a time series, *i.e.* sensor readings vs. time
- Data covers a time span of several years
- Data is multidimensional, as reading from a number of control sensors are considered
- Data is taken as it is, covering everything that has been recorded, *i.e.* cold and hot start-ups, urgent and scheduled shutdown, sensors failures and other uncertainties
- Time location for state shifts, unit shutdowns, etc. is unknown

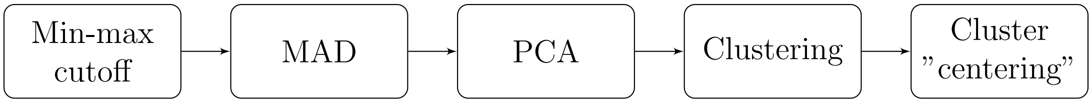


Figure 5.2: Industrial data processing sequence

So below we are proposing a way to recover information about steady states of industrial ammonia converter operation from data for several years. In order to clean it from uncertainties, it is treated both ways - with respect to the process history (as time-series), and regardless of it. So, in order to single out the steady state from the data of a given quality, we have done the procedure shown on Fig. 5.2. The data is sequentially fed through the following step in order to get cleaner process data.

Min-max cutoff. It constitutes the most basic preliminary data cleaning. For some sensors one can define a “feasible” range of measurements as minimum and maximum values. Beyond this range the readings no doubt will be irrelevant to normal unit operation. For example, if unit pressure is around atmospheric, it means that likely unit has been shutdown and depressurized for maintenance thus any reading at that time has can be safely neglected. The same can be defined for temperature, as catalyst operation range is define by manufacturer and know.

MAD. *Median absolute deviation* (MAD) filter is a technique widely used in signal processing to deal with burst signal disturbances. In given time series data set $\mathbf{x}$, for point x_t at time t one can define a window of width k and find corresponding median μ (Fig. 5.3). Then an absolute deviation for each point within a window from median is calculated (MAD). If point x_t deviates from median of median further than some threshold value, then it is treated as outlier and shall be removed[36]. The moving window is applied to entire time series data for each sensor independently. This way allows for removal of data points which were unable to be detected by min-max cutoff.

PCA. *Principal component analysis* (PCA) is a method of data transformation based on variance in original data. PCA projects original data set $D_{m\times n}$ (m data entries of

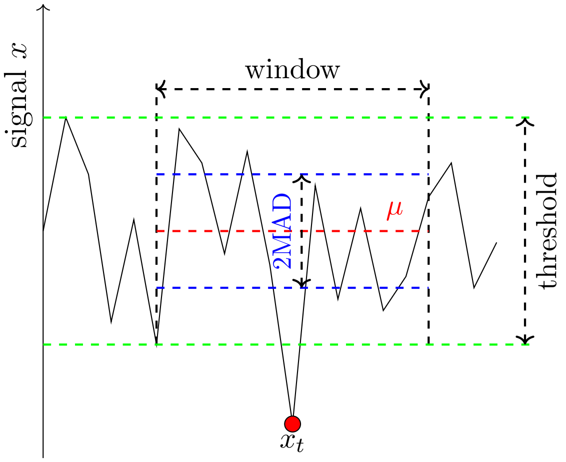


Figure 5.3: MAD filter

dimensionality n) onto new set of orthogonal basis vectors u_i, often called as *principal components*, such that the variance of projected data is maximized[37]. Therefore, each original data point can be exactly given as linear combination of principal components. The detailed description can be found elsewhere[38]. Thus, each original data point can be approximated as a linear combination of first d principle components ((5.8)). By doing this, one is able to reduce dimensionality of data while preserving the most of its information. Also, it help to reduce noise and correlations in original data.

$$x_i \approx \tilde{x}_i = \sum_{i=1}^{d} \beta_{ni} u_i, \quad d < n \tag{5.8}$$

For example, let us have a data set of two variables (Fig. 5.4). The original axis are given in black. Applying PCA, one can rotate original axis such that new axis PC1 will be directed along with maximal variance in data, PC2 will be orthogonal to PC1 and with second largest variance (in green). Knowing the transformation rule it is always possible to restore original data from principal components. Therefore, after moving to a new basis, one can just use PC1 to approximate a point in 2D space. For higher dimensional case, one can select first d principal components based that cover required variation in data space.

Clustering. Clustering is a process of splitting a data set into number of groups based

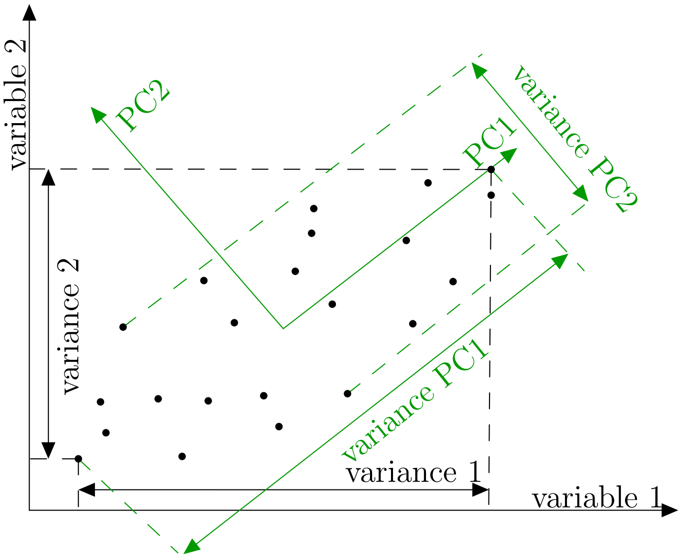


Figure 5.4: PCA transformation

on their proximity to each other[39]. The measure of "proximity" can be defined differently depending on data domain using different metrics[38]. Therefore, one can say that points with a particular cluster are more resemble to each other than to any point in other cluster. Thus, after data was cleaned from outliers and correlated noises over three previous steps, this approach can be applied towards splitting a process history data points based on their affiliation with different steady states. As process conditions belonging to the same state will be closer to each other, one can use Euclidean distance to define proximity of points ((5.9)). A vast number of clustering methods The number of clusters k can be found by minimization of within cluster sum of squares ($wcss$) - sum of distances from each point in cluster x_i^k to its center among all clusters x_{center}^k ((5.10)).

$$d_{x_1-x_2} = \sqrt{\sum_{i=1}^{n}(x_i^1 - x_i^2)^2} \tag{5.9}$$

$$wcss = \sum_{j=1}^{k}\sum_{i=1}^{p_j} d_{x_i^j - x_{center}^j} \tag{5.10}$$

where n - dimensionality of data point, p_j - number of points in ith cluster. Obviously, the minimum for (5.10) will be when number of cluster is equal to number of data point ($k = m$) and is exactly equals to zero. So the number of clusters is found when incremental reduction of $wcss$ is becoming negligible with increasing number of clusters. Thus, one can calculate $wcss$ for $k = 1 \quad \text{to} \quad m$, and stop search when reduction in $wcss$ is less than 10%. In this work we used and compared two clustering methods - *kmeans* and *kmedoids*. Detailed description can be found elsewhere.

Cluster drop off. As we are striving to find major distinction and isolate steady states from cluster data, the intention of this is to find some "middle ground" in cluster structure. This is done by removing points located "far away" from cluster center. Thus, for each point in cluster i one can calculate Euclidean distance to the center and drop off the upper quantile q from consideration as being the most ouliering points in the group ((5.11)). Authors used $a = 0.5$, thus removing upper half of points.

$$\begin{aligned} D &= \{d_{x_i^j - x_{center}^j}\} \quad for \quad i = 1 - p_j \\ q(a) &= \{d \mid Pr[D \leq d] = a\} \end{aligned} \tag{5.11}$$

5.4 Data and methods

In this work we used industrial data collected from the ammonia plant for the period of 14 years. All instrumentation data is taken as daily average yielding the raw data set with 5000 observations. Catalyst bed temperature originally was measured by three termocouples located radially either at bed's entrance or exit, but average of three measurements was used in the model fitting. Gas chromatography (GC) analysis were performed every 3-4 days. At model fitting stage, entire processed data set was used, but on validation stage - only those days with GC analysis were selected.

The converter model is implemented using R language[40]. The diffusion equation (2.5) is solved using orthogonal collocation method for spherical geometry[41]. Mass and energy balance equations ((5.7)) soled with Runge-Kutta 5th order. Industrial data analysis procedure is also developed in R. MAD filter is taken from *pracma* package as function *hampel*[42].From *stats* package: PCA as function *prcomp*, kmeans clustering as function *kmeans*, partitioning around medoids are function *pam*.

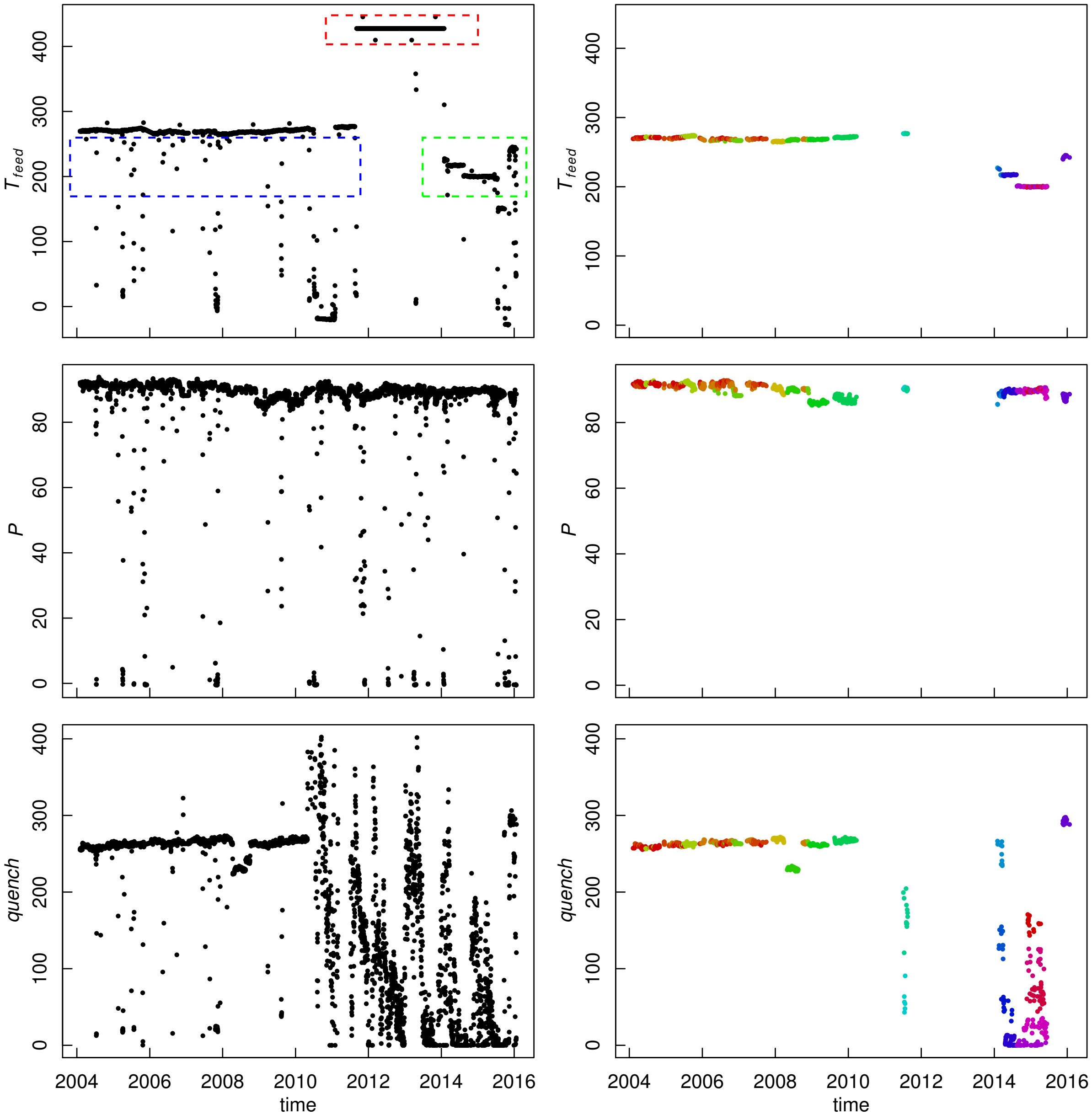
5.5 Results and discussion

5.5.1 Data cleaning

In order to analyze process performance authors chose five main converter control parameters - feed temperature, process pressure, volumetric feed rate, volumetric flow rate for quenches - having 5 in total. Using examples from few sensors we are willing to illustrate the contribution of each stage to data cleaning. Fig. 5.5(a) shows untreated industrial data over years for the three control parameters - T_{feed}, P, $quench$. Fig.5.5(b) shows results of data cleaning from all stages. One can see that points are less scattered and grouped in accordance with proximity to each other, thereby resembling a steady state modes of operation. It is evident that data in Fig. 5.5(b) is cleaner and more clear. Moving from (a) to (b) one can easily distinguish operation modes at which the unit was operating over a period of time.

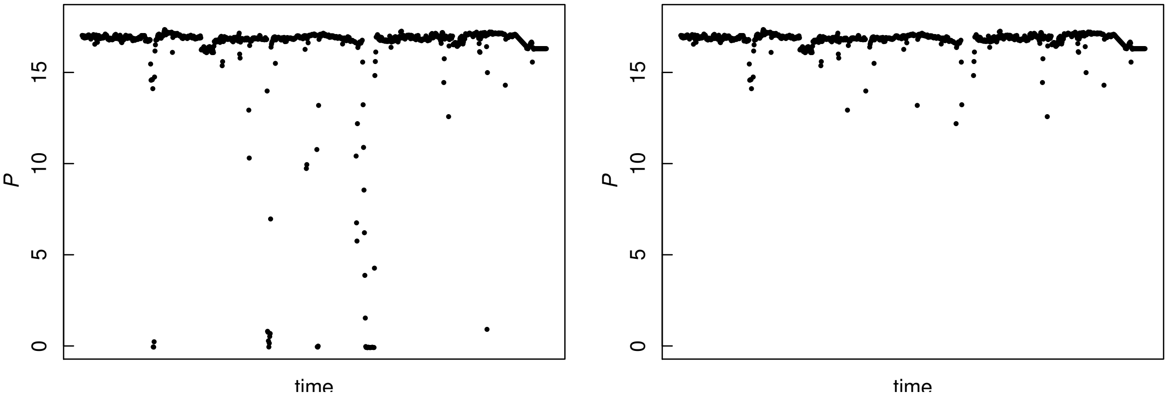
Now we provide more in-depth explanation of each step and its contribution into data cleaning. Fig. 5.6(a) shows untreated industrial data. Min-max cut off allow for points remove which are obviously does not correspond with process conditions at steady states. Fig. 5.6(b) show removing lower portion of data corresponding with non-operational times. However, some singleton points are still presented in the graph. Then, applying MAD filter one can remove those points as well, which correspond to short-time changes in sensor signal due to failure, unexpected start up and so on. Fig. 5.6(c) depicts data after MAD cleaning where those points are removed.

Notably, that if one does not use either of two step, the effect would be unreachable. For example, if one excludes min-max cut off, it would be impossible to remove portion of data, which corresponds to the long time sensor failure and shown in red rectangle at the

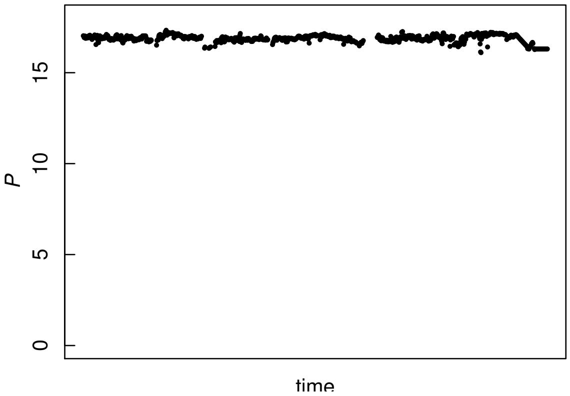


(a) Raw sensor signal (b) Cleaned and clusterized data

Figure 5.5: Process data



(a) Raw pressure data (b) After min-max cut off



(c) After MAD filter

Figure 5.6: Effect of Min-max cut off and MAD filter on process data

top of Fig. 5.5(a) for T_{feed}, by MAD filter only. On opposite, if one only uses min-max cut off, one will not be able to remove data in blue rectangle on the same figure. Since those points have higher values than group of points in green rectangle and belonging to feasible operation range. Thus, they will remain untreated.

Once data was treated from outliers, we applied PCA to the remaining data points, and performed clustering of first two principal components. We used two popular clustering algorithms - *kmeans*[36] and partitioning around medoids or kmedoids[43]. In order to find the number of clusters, we evaluated reduction in *wcss* with increasing k. Firstly, we used *kmeans* algorithm for number of clusters 1 to 100 (Fig. 5.7 (a)). However, it did not perform well enough to determine number of clusters. One can see that reduction in *wcss* is uneven and non-monotonous with increasing k. From Fig. 5.7(b) one can see

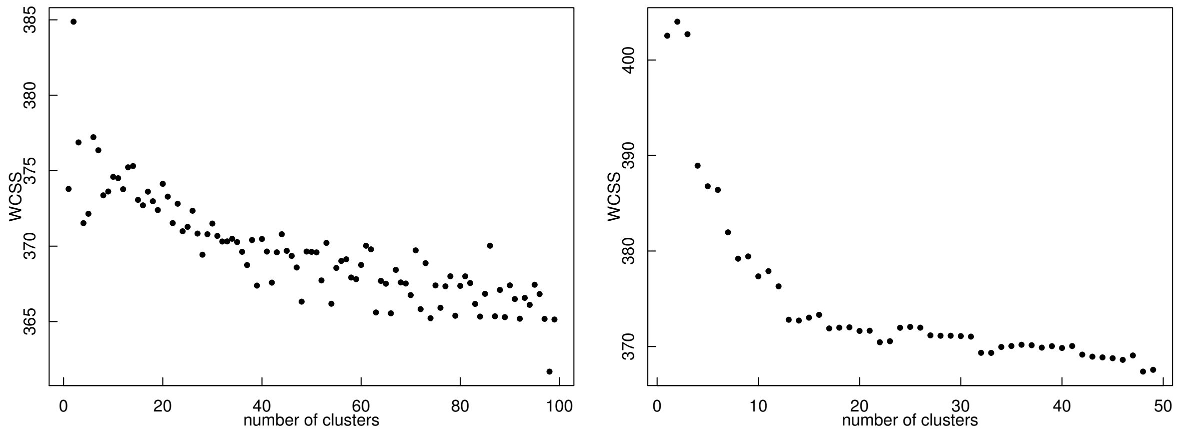


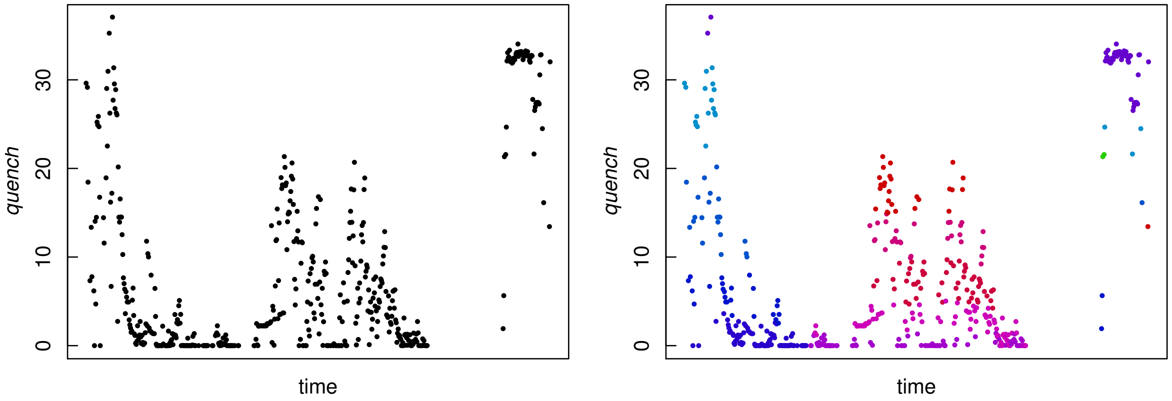
Figure 5.7: WCCS reduction with number of clusters

that *kmedoids* converges better than *kmeans*. Reduction in *wcss* is more distinct and monotonous, and approximately after $k \approx 20$ is becoming negligible. The final number of clusters 21 is chosen for further analysis.

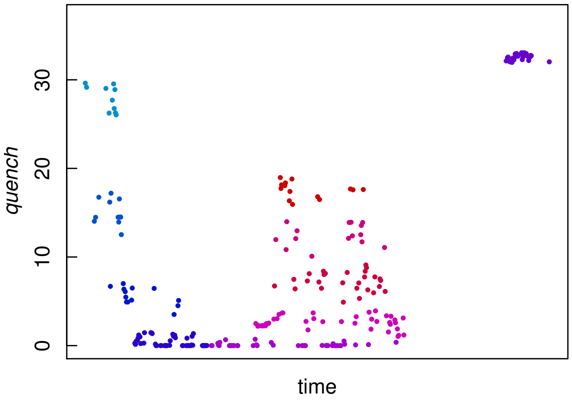
The data for *quench* before and after clustering is shown at Fig.5.8(a) and (b) respectively. The effect of clustering is especially notable with process parameters which has been changing more frequently and data points look scattered, as shown in the figure. One can see that quenching values has been widely fluctuating with time, so any lengthy steady periods are barely distinguishable. One can see data points grouped by colouring after clustering was applied. Further, Fig.5.8(c) shows only points left after removal of the upper 0.5 quantile. One can see that data became less scattered with distinguishable operating modes. This drop off within a cluster allows for removal of outliering points, therefore determining points "around the center" as the best representation of steady state.

5.5.2 Model fitting and validation

The clean industrial data was further used for model fitting and validation. In order to do it, authors minimized the sum of squared distances between measured and simulated temperatures for each bed ((5.12)) as function of kinetic constant. The model fitting



(a) Before clustering (b) After clustering



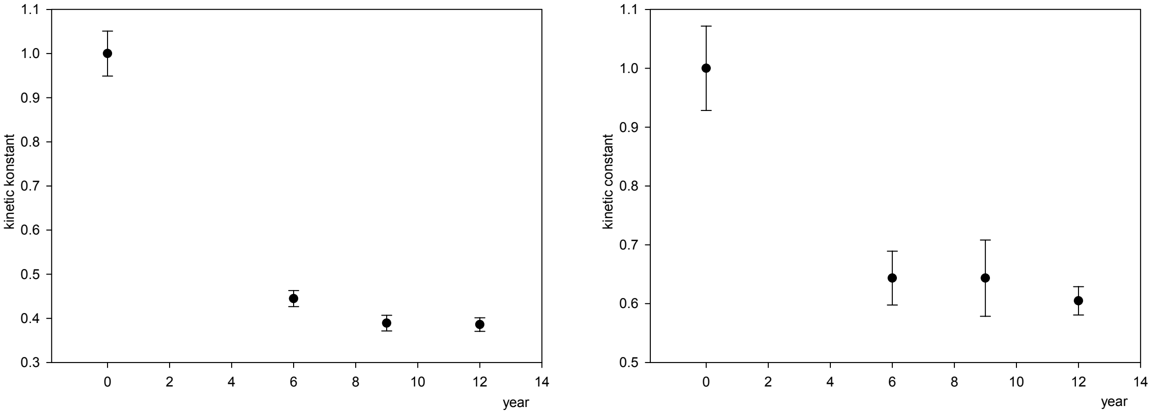
(c) After cluster centering

Figure 5.8: Effect of clustering on data cleaning

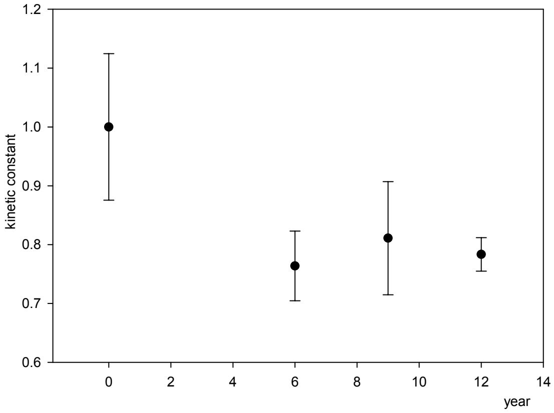
was done for a groups of point taken over distant time periods. As loaded catalyst is a mixture of several different sub brands in certain ratio, we obtain three kinetic constant being a representation of each bed independently.

$$min \quad f(k_1, k_2, k_3) = \sum_{i=1}^{3} (T_{bed_i}^{simulated} - T_{bed_i}^{observed})^2 \tag{5.12}$$

Results of model fitting vs. catalyst life time are shown in Fig. 5.9. One can see that catalyst activity is gradually decreasing over time. The most of deactivation is occurring within first few years of operation. Unfortunately, due to unavailability of the data with that time span (years 0 to 6), we cannot specifically determine the rate of deactivation.



(a) Bed 1 (b) Bed 2



(c) Bed 3

Figure 5.9: Ammonia catalyst deactivation over time

However, it is evident that apparent value of kinetic constant in the beginning of catalyst cycle is higher than the ones closer to an end. Comparing catalyst deactivation among different beds we can say that deactivation rate is decreasing with increasing bed number. After first few years of reduction in catalytic activity, it reaches plateau and remain constant. If for beds 1 and 2 it takes more than a half of total cycle length to reach it, but for catalyst in bed 3 it is happening sooner. Results show no significant changes in kinetic constant k_3 over latter time span (years 6 to 12). However, actual deactivation might still be happening, it is hardly unnoticeable within industrial unit and the data does not reflect those changes.

The model validity was asses by comparing experimental and simulated temperature profiles at catalyst bed inlet and outlet. It was found that model is in good agreement with industrial data (Fig. 5.10). The error for temperature is around 4%. Moreover, one can compare between simulated and experimental feed compositions (Table 5.1). The model gives a good match in stream composition as well. The product gas composition was not used in the fitting, but it showed a very good consistency with experimental data. It provides enough assurance in model quality and its applicability to process optimization.

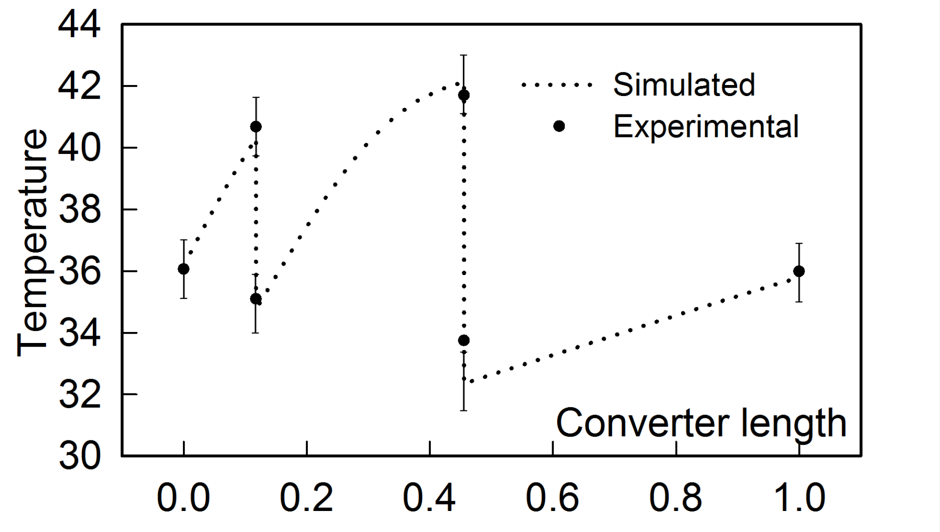


Figure 5.10: Simulated and experimental temperatures within ammonia converter

Gas stream composition

	N_2	H_2	NH_3	CH_4	Ar
simulated	3.77	9.02	2.13	-	-
experimental	3.70	9.04	2.17	-	-

Table 5.1: Comparison between simulated and experimental gas compositions

5.6 Multi-objective optimization of ammonia converter with catalyst deactivation

In order to conduct a multi-objective optimization one needs to identify *a)* industrially important objectives, *b)* select key process control parameters and *c)* define a search domain, *i.e.* box-constraints for controls (upper and lower bounds) or other constraints on process performance parameters if any.

Definitely, one of the most important criteria of converter operation is ammonia production. The efficiency of ammonia production is expressed in its molar fraction if converter effluent X_{NH_3}. Ammonia synthesis reaction (2.1) is highly exothermic, generating large amounts of heat per bed pass. Depending on converter design and unit layout, the heat can be removed through feed pre-heat, quenching, stream generation, etc. As actual process scheme remains unknown to the reader, we are introducing another performance criterion of converter operation as amount of regenerated heat HR - heat which was recovered within the unit. This performance criterion is a measure of heat efficiency, as more heat is not wasted and used elsewhere on a plant.

Control-wise, through model sensitivity analysis and engineering consultations we chose three parameters with largest contribution into process performance. They are: feed temperature T_{feed} and quench-to-feed ratio QFR, also converter pressure P has a great impact on X_{NH_3}, but it is not as easily changeable as other two. Minimum and maximum bounds for control parameters are set in accordance with industrial practice. Pursuantly with catalyst specification, we also add constraints for each bed maximum temperature in order to prevent catalyst from damaging.

Thus, we will consider two MOO cases to investigate possibilities for process performance improvement. Especially, we will consider effect of catalyst activity. As has been shown above, the deactivation occurs more rapidly within first few years, while staying relative constant in second half of lifetime. Thus, we will consider two catalyst stages -

fresh and *old*. Former being a representation of fresh catalyst, just loaded into converter, while latter - being close to the end of cycle.

The formulation of MOO problem is the same for both cases as show in (5.13). The difference is in control parameters. For case *fresh* we use T_{feed} and QFR as main variables and solve MOO at two different pressures. The pressures are chosen that lower one is a representation of the most common loop pressure obtained from process history and more specific for operation with fresh catalyst. The higher one is chosen to illustrate an opportunity to alter loop pressure to boost up ammonia but still remains within feasible range.

MOO formulation: In summary, one can formulate multi-objective optimization problem for up mentioned cases as follows:

$$\begin{aligned} &maximize \quad I_1(\mathbf{x}) = X_{\mathrm{NH_3}}^{out} \\ &maximize \quad I_2(\mathbf{x}) = \mathrm{HR} \end{aligned} \tag{5.13}$$

$$\text{subject to:}$$

$$T_{bed}^{out} \leq T_{max} \quad for \quad each \quad bed$$

$$\mathbf{x} = T_{feed}, QFR \in [min; max]$$

5.6.1 MOO results

The Pareto optimal set for *fresh* case is shown in Fig.5.11. One can see the wide range of compromising solution to select the best operating conditions to serve his/her purpose. Relative variation in heat recovery is around 7, while ammonia production ranges at 0.08.

Generally, high temperatures and QFR are favourable for ammonia production. A proper control of both parameters at the same time will allow the unit to operate at the optimal state. Moreover, the same conditions at higher pressures are able to provide more ammonia. The entire Pareto set for higher pressure is on the right from lower having any point in it with better X_{NH_3}.

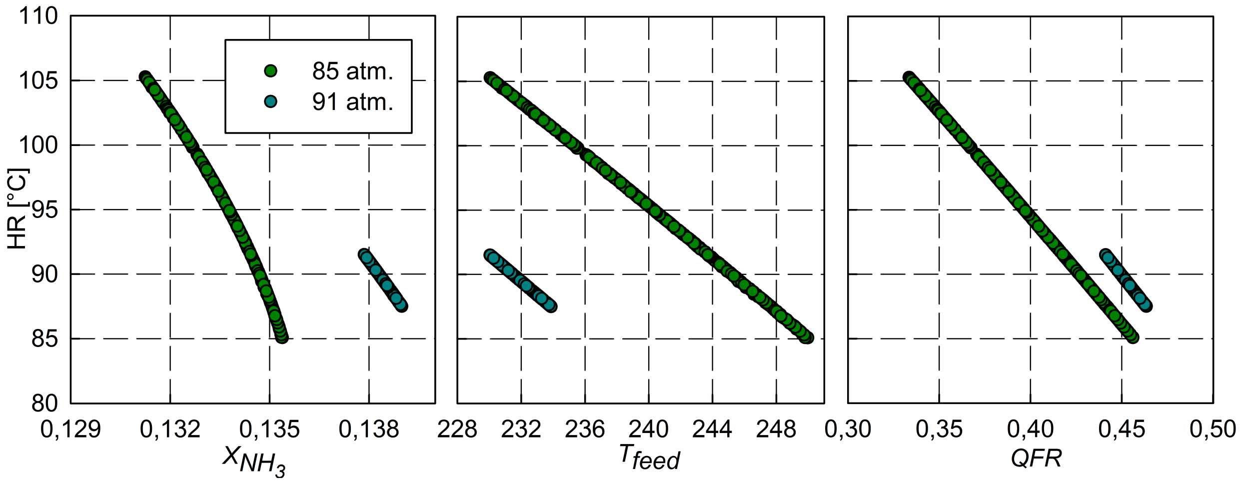


Figure 5.11: Pareto optimal set of solutions for case *fresh*
Figure a) shows both objectives. Figures b), c) shares the same Y-axis with figure a) and shows relation of process parameters to Pareto-optimal set of objectives.

However, higher pressure provide much lower range of optimal solutions. Contrary to ammonia production, higher pressure on average provide lower heat recovery possibilities. The is due to faster reaction rates at higher pressure, when more heat is produced and temperature constraints come in greater effect. Also, quenching effect is becoming less noticeable and major adjustments in converter operation has to be done with T_{feed}.

Further one can look into Pareto set of solutions for case with *old* catalyst (Fig. 5.12). Evidently, one can note that on average converter performance decreases by the end of catalyst life - both production and heat recovery wise. Ammonia production is between 1.88 - 1.97 and heat recovery - 21 - 30 (vs. 2.08 - 2.22 and 29 - 35 for *fresh* respectively). However, if one consider only high pressure, the range increases comparing with *case*.

Firstly, pressure increase is essential for less active catalyst to boost up ammonia production. Comparing tow cases at pressure 10, one can see that relative reduction is over 10%. This is significant drop, thus in shall be compensated with not only T_{feed} and QFR, but with system pressure as well. Also, since X_{NH_3} is decreasing with time, the HR should be of a lesser concern as it is becoming more important to keep sufficient ammonia.

Secondly, the optimal feed temperature increases drastically from 20.8 - 22.8 to 23.7 -

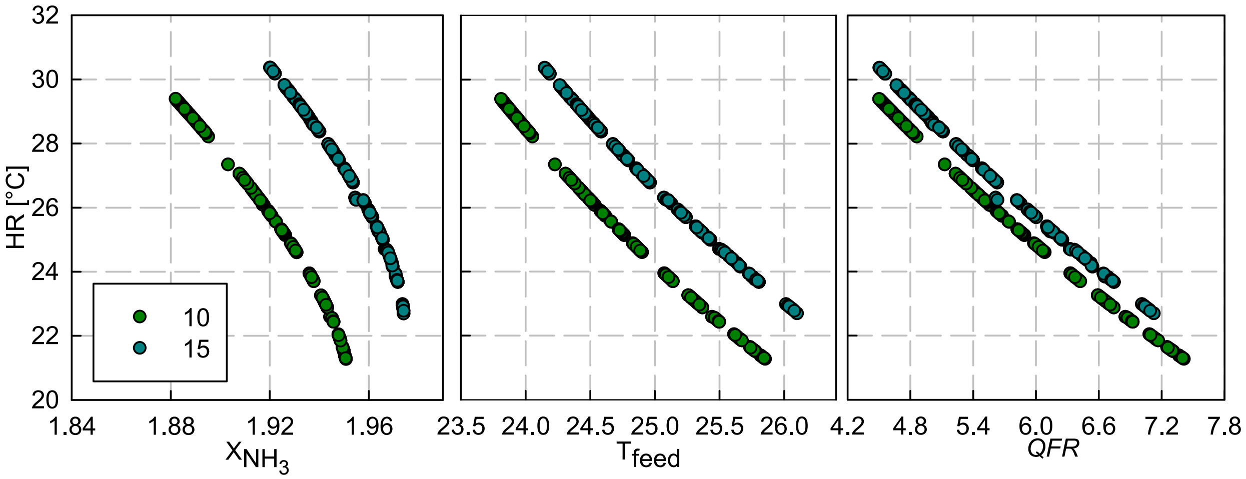


Figure 5.12: Pareto optimal set of solutions for case *old*

26.1. Noticeably that ranges do not overlap, thus making it almost impossible to maintain sufficient ammonia production or heat recovery at the same feed conditions.

Notably that at case *old*, shift from pressure 10 to 15 improves both objectives and Pareto correspondingly shifts to the right. Contrary, the opposite effect can be seen with fresh catalyst, when Pareto shift to the left. It can be explained as with less active catalyst one still have room to increase reaction rate without violating constraint, while with more active catalyst increase in converter pressure has to be compensated with lower T_{feed}.

QFR range is a wider for *old* catalyst (4.2-7.4 vs 4.8-7.0). However, optimal quench-to-feed ratio is almost the same for two different pressure as difference is quite negligible. Thus for old catalyst, temperature has to be adjusted with higher attention that quench when increasing pressure loop.

Therefore, the main process operation features with respect to catalyst life are (Fig.5.13):

- Ammonia catalyst is slowly but steadily deactivating, reducing production by 10%
- One can compensate for reduction of activity by proper adjustment of P, T_{feed} and QFR
- Converter pressure has to be increase along with catalyst life

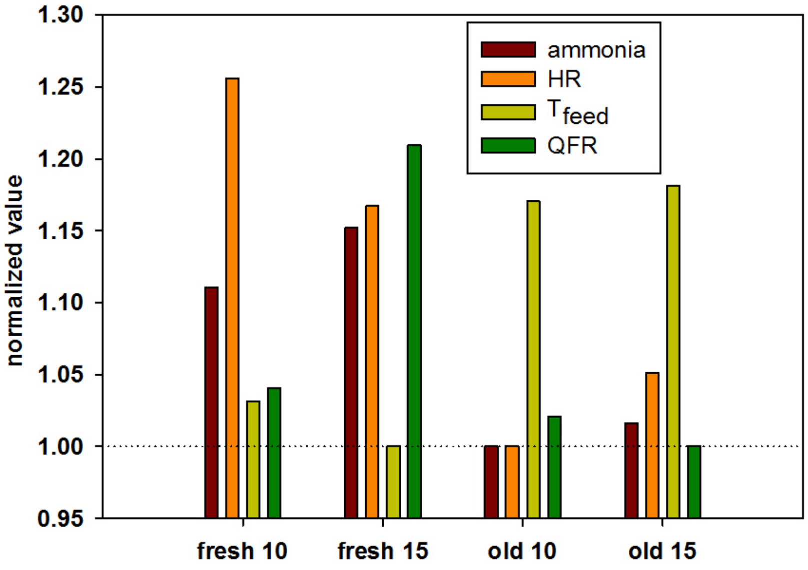


Figure 5.13: Comparison for “middle” points in pareto sets

- Proper pressure for the fresh catalyst has to be adjusted carefully as one may face excessively high temperatures inside bed
- Feed temperature increase is also essential with time as it is impossible to keep sufficient ammonia production

5.7 Summary and conclusions

In this work authors performed a multi-objective optimization study of an industrial ammonia converter. We used a developed first-principle mathematical model in order to *a)* estimate apparent kinetic constant of the catalyst at industrial conditions and *b)* perform simulations for MOO. Catalyst kinetics were estimated using industrial data for a time span of several years. Since original industrial data is subject to noise, uncertainties, etc., it cannot be used directly and has to be cleaned. We proposed a method of industrial data treatment around steady states of converter operation. By doing this we were able to estimated catalyst deactivation with respect to time.

Results of MOO showed the necessity of both feed temperature and pressure increase by the end of catalyst life. Without either it is impossible to keep sufficient ammonia production, thus proper control of these two parameters is essential. For fresh catalyst, it is possible to utilize lower unit pressure thus saving on compression and self-supplied heat. Contrary for old catalyst ammonia production is of higher importance, therefore optimal range of operation in Pareto has to be shifted towards it.

Nomenclature

AIC	Akaike information criterion
bed	refers to catalyst bed
C	total concentration of components [kmol/m^3]
C_p	specific heat capacity [kJ/kgK]
D_{ie}	effective diffusivity of component i [m^2/s]
$feed$	refers to process gas feed into the converter
f_i	fugacity of i$^{\text{th}}$ component
F_{N_2}	molar flow rate [mol/s]
HR	heat recovered through heat recovery system
K	overall heat transfer coefficient [W/m^{2}K]
k_2	kinetic constant of reverse reaction [kmol/m$^3 \cdot h$]
K_a	equilibrium constant
l	length coordinate for interchanger [m^2]
L	interchanger length [m^2]
MAD	median absolute deviation
$\dot{m}_i$	mass flow rate [kg/s]
out	refers to a catalyst bed out
P	converter pressure [atm.]
q	quantile
Q	volumetric rate [m^3/s]
QFR	quench-to-feed ratio

quench	refers to converter quench
r_i	tube radius [m]
R_{NH_3}	rate of ammonia formation [kmol/m$^3 \cdot$ h]
R_p	radius of catalyst particle [m^2]
T	gas temperature [°C]
t	time
V	bed volume [m^3]
wcss	within cluster sum of squares
X_i	molar fraction of component i

Greek letters

α	constant parameter for reaction equation
μ	median value
ν_i	stoichiometric coefficient in Eq. 2.1 for component i
χ	nitrogen conversion
ω	dimensionless distance from pellet center to interior point
ΔH_R	enthalpy of reaction [kJ/kmoleK]
ϵ	bed voidage
ϕ_i	fugacity coefficient of component i
η	effectiveness factor

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Chapter 6

Conclusion

6.1 Conclusions

Multi-objective optimization approach is an effective tool for improvement of process performance in chemical engineering. It is especially efficient in application towards industrial processes as they usually bare more than one conflicting objective. Therefore, it allows to account for a number of them often yielding a more efficient solution.

Throughout the thesis, multi-objective optimization study of industrial ammonia synthesis converter is considered.The work was done in collaboration with plant engineers and operators who provided me with valuable guidelines on plant operation. As a result, accurate first-principle mathematical model for ammonia converter was developed and used in multi-objective optimization context to investigate ways of the plant improvement.

In chapter 1, the model development for converter is described. The converter of this particular design has not been reported in the literature before. Thus a proper investigation of plant and unit layout, process data was required to provide a valid model. The model combines heterogeneous gas-solid diffusion reaction in porous catalyst with one-dimensional plug flow. Also, heat transfer between process gas and converter feed in interchanger is modelled as well. Important to note that the model and its part are able to be used for different converters. The applicability range requires converters to be with recycle and have some ammonia in the feed to avoid numerical errors in kinetic rate equation. Also, if it happends that for some catalyst support has low heat conductivity, isothermal effectiveness factor no longer apples and one has to add one more equation for heat transfer within catalyst pellet. Lastly, model best work for beds with behavious close to plug flow. Thus, they have to operate under high gas velocities and have greater lenght than diameters.

The model was validated with industrial data and showed good consistency with experimental results. The sensitivity analysis has followed to estimated effect of process parameters on process performance and find most important ones.

In chapter 2, two MOO case studies on the converter was performed. All results were achieved using Eureqa® as surrogate model trainer paired with NSGA-II as on optimization method. In first case, higher ammonia production and better heat recovery in the unit was targeterd. Results yielded a Pareto set showing possible option to choose operating conditions from. It was revealed that along with increased ammonia production it is also possible to introduce some heat savings through better heat recovery and bring converter's inlet feed temperature down.

Chapter 3 considers an attempt to approach industrial process data and its use for modelling. Carbon dioxide removal from ammonia synthesis gas within Selexol unit wastudieds. Real industrial data was used to provide statistical model and use it for process optimization. Process modelling was done based on weighted linear regression in conjunction with data clustering. It was possible to select the most relevant feature which affect performance of carbon dioxide removal unit and propose better operating point for Selexol recovery. The method of data modelling showed itself efficient to some extend, however, still suffers from outliers present in data.

In chapter 4, optimization study of ammonia converter under catalyst deactivation is considered. The same model as in chapter 1 was utilized for simulation. Preceding optimization study, the method of data analysis from chapter 3 was reconsidered and improved to be used along with first principle model to estimated catalyst kinetics. The method was significantly improved and allowed to provide good results. Catalyst degradation was observed from industrial data and the model was fitted with it in order to estimate catalyst kinetics at different time periods. The converter optimization with respect to catalyst deactivation yielded Pareto optimal solution which indicated decay in converter performance. Still it was possible to maximize losses due to deactivation as well as provide ways to decrease heat duty of converter at earlier stages of catalyst operation.

6.2 Recommendations and future work

Considering promising outcome of the work, it is neccessary to do some more in depth studies to justify feasibility as follows:

- Economic evaluation of Pareto optimal solutions to find better operational point business-wise
- Modefy bed model from axila to radial flow and inestigate possibilities for improvement through changing converer design
- Perform CFD modelling of flow pattern inside catalyst bed to have more accurate knowledge about radial temperature distribution
- Modify model fitting procidure trough creating a feedback from the model to the quality of data points selected by the cleaning algorithm
- Create automatic surrogate generation and exclude one from doing it manually

Appendix A

Heat transfer model for interchanger

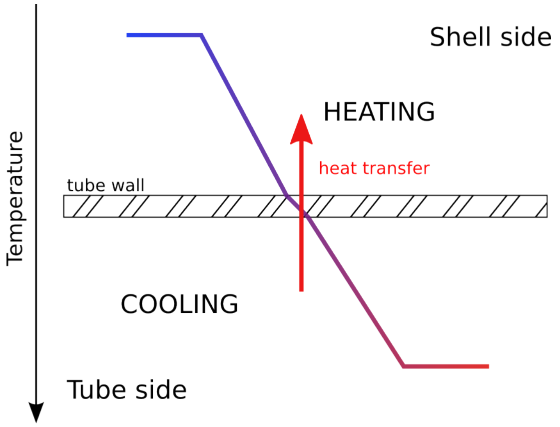

Figure A.1: Heat transfer along tube wall

Th following boundary problem is solved:

$$\text{Shell side}: \quad \frac{dT_{shell}}{dl} = \frac{2\pi K(T_{tube} - T_{shell})}{\dot{m}_{shell} C_{p_{shell}}}$$

$$\text{Tube side}: \quad \frac{dT_{tube}}{dl} = -\frac{2\pi K(T_{tube} - T_{shell})}{\dot{m}_{tube} C_{p_{tube}}}$$

$$K = \left[\frac{1}{\alpha_{tube} r_{inner}} + \frac{1}{\lambda}\frac{1}{\alpha_{shell} r_{outer}}\right]^{-1}$$

subject to boundary conditions:

$$l = 0: \quad T_{shell} = T_{bed1}^{inlet}$$

$$l = L: \quad T_{tube} = T_{bed2}^{outlet}$$

where K - overall heat transfer coefficient [W/m^{2}K], α_i - convective heat transfer coefficient towards tube wall from shell or tube side [W/m^{2}K], r_i - inner or outer interchanger tube radius [m], λ - thermal conductivity of interchanger material [W/mK], l - length coordinate for interchanger integration [m], L - interchanger length [m].

With α_i for either side found as:

$$\alpha_i = \frac{\mathrm{Nu} \times k}{d_{pipe}}$$

where, Nu - Nusselt number, k - thermal conductivity for fluid [W/mK], d - corresponding pipe diameter [m]. Nusselt number:

$$\alpha_i = \frac{\mathrm{Nu} \cdot k}{d_{pipe}}$$

$$\text{Heating :} Nu = 0.0243\mathrm{Re}^{0.8} Pr^{0.4}$$

$$\text{Cooling :} Nu = 0.0265\mathrm{Re}^{0.8} Pr^{0.3}$$

$$\mathrm{Re} = \frac{v d_e \rho}{\mu}$$

$$\mathrm{Pr} = \frac{C_p \mu}{k}$$

where Re - Reynolds number, Pr - Prandtl number, C_p - heat capacity of fluid [J/molK], μ - dynamic viscosity [$\mathrm{Pa} \cdot \mathrm{s}$], v - linear flow velocity, d_e - equivalent diameter of tubes, ρ - flow density [kg/m^3].

Curriculum Vitae

Stanislav Ivanov

HIGHLIGHTS

- Overall 6 years of experience in developing models for chemical processes and plants, performing simulations and conducting operation and design optimization
- Experience in model development using commercial simulators as well as creation of custom modelling tools with programming languages
- Extensive practical skills and knowledge in mathematical methods used in process modelling and numerical optimization along with their applications towards chemical processes
- Experience in dealing with large multidimensional data, performing analysis, data mining and various statistical methods, data visualization
- Strong analytical and troubleshooting thinking
- Outstanding track record in communication with academic and engineering audience
- Excellent team player with demonstrated leadership skills

EDUCATION AND RELATED EXPERIENCE

- PhD in Chemical Engineering, Western University, London, Canada
  Supervisor: Dr. Ajay K. Ray, Professor and Department Chair
  January 2013 – April 2017
  Thesis: Multi-objective optimization of an industrial ammonia synthesis
  - Developed first principle model for a gas phase catalytic industrial converter in collaboration with CF Industries (Sarnia, ON). Model encompasses gas-solid reaction with diffusional resistances, heat transfer model for converter design and catalyst deactivation
  - Developed statistical method for study of catalyst deactivation from industrial data
  - Implemented software package for the converter simulation and optimization
  - Performed several optimization studies aiming to increase converter performance
  - Used methods of statistics and machine learning to model operation of packed bed absorber and troubleshoot its performance

- Visiting graduate student, University of Waterloo, Waterloo, Canada
  May – June 2015, Dr. Ali Elkamel's research group
  - Received a training in machine learning methods and chemometrics
  - Worked on a project for biodegradability prediction of chemical compounds

- Teaching Assistant in Chemical Plant Design course
  September 2014 – PRESENT
  - Supervised groups of undergraduate students
  - Assisted in process flow diagram, P&ID development
  - Consulted students for equipment design, i.e. catalytic reactors, distillation columns, heat-exchangers, etc.

- Assisted in process simulation and optimization with Aspen HYSYS and VMGSim

▪ MSc in Chemical Engineering, Tomsk Polytechnic University, Tomsk, Russia
September 2010 – June 2012
Thesis: Process modelling for regeneration of Pt-catalysts for naphtha reforming and alkanes dehydrogenation

- Developed thermodynamic model of oxidative chlorination of Pt-catalyst
- Implemented software for regeneration monitoring, control and optimization
- Troubleshot catalyst regeneration at naphtha reforming unit resulted in successful star up and long catalyst life
- Participated in kinetic model development for catalytic reactors at linear alkylbenzene plants - Pacol, DeFine processes
- Registered software patent for water supply optimization program

▪ Engineering Intern, HF Alkylation Unit, PO Kirishinefteorgsintez Ltd., Kirishi, Russia
July – August 2011

- Collected data and analyzed unit operation for development of mathematical model
- Performed unit simulation and optimization studies

▪ Engineering Intern, Platforming Unit, Gazpromneft, Omsk, Russia
June – July 2009

▪ BSc in Chemical Engineering, Tomsk Polytechnic University, Tomsk, Russia
September 2006 – 2010
Field of study: Petroleum refining and petrochemistry

PUBLICATIONS

1. Stanislav Y. Ivanov and Ajay K. Ray Multi-objective optimization of industrial ammonia converter under catalyst deactivation. *Ready for submission*
2. Stanislav Y. Ivanov and Ajay K. Ray Modelling and multi-objective optimization of industrial ammonia converter. *Ready for submission*
3. Stanislav Y. Ivanov, Irena O. Dolganova, Evgeniya V. Frantsina, Elena N. Ivashkina, Emiliya D. Ivanchina Increasing the Selectivity of Synthesis Stages for Linear Alkyl Benzenes, *Current Organic Synthesis*, vol. 14 (3), pp. 353-364, 2017
4. Stanislav Ivanov, Natalia Belinskaya, Emilia Ivanchina, Galina Nazarova, Elena Ivashkina The Increase in the Yield of Light Fractions During the Catalytic Cracking of C13-C40 Hydrocarbons, *Current Organic Synthesis*, vol. 14 (3), pp. 342-352, 2017
5. Matthew J. Palys, Stanislav Y. Ivanov, Ajay K. Ray Conceptual Approach in Multi-Objective Optimization of Packed Bed Membrane Reactor for Ethylene Epoxidation Using Real-coded Non-Dominating Sorting Genetic Algorithm NSGA-II *International Journal of Chemical Reactor Engineering, 2016*
6. Zhefu Liu, Linzhou Zhang, Ali Elkamel, Dong Liang, Suoqi Zhao, Chunming Xu, Stanislav Y. Ivanov and AjayY K. Ray Multiobjective Feature Selection Approach to Quantitative Structure Property Relationship (QSPR) for Predicting the Octane Number of Compounds Found in Gasoline. *Under review*

7. Zhe F. Liu, Hedia Fgaier, Stanislav Y. Ivanov, Ali Elkamel, Xiang H. Meng, and Suo Q. Zhao A Novel Hybrid Feature Selection Methods and Prediction for Ready Biodegradibility of Chemicals Using Random Forests and Boruta *International Journal of Technical Research and Applications*, 2015
8. Stanislav Y. Ivanov, Ajay K. Ray Application of multi-objective optimization in the design of industrial catalytic reactors. *Chapter in* ***Catalytic Reactors***. Edited by B. Saha. DeGruyter, 2016
9. Stanislav Y. Ivanov, Ajay K. Ray Multiobjective Optimization of Industrial Petroleum Processing Units Using Genetic Algorithms, Procedia Chemistry, 2014, Vol. 10, p.7-14
10. Stanislav Y. Ivanov, Igor K. Zanin, Elena N. Ivashkina, Emilia D. Ivanchina, Anatoly V. Kravtsov Regeneration process modeling of Pt-catalysts for naphtha reforming and dehydrogenation of higher paraffins, Bulletin of Tomsk Polytechnic University, 2010, Issue 319, Vol. 3, p. 96-99

HONORS, AWARDS AND CERTIFICATES

Excellence in teaching	Western University	2016
Runner up	Research Bridges Conference	2016
Finalist, 3rd award	All-Russian Exhibition of Students Research Projects	2011
Scholarship	Government of Russian Federation	2011
Software licence certificate		2011

TECHNICAL SKILLS

- Proficient in **programming**. Languages: R, C/C++, LaTeX
- Experienced in using various engineering software such as **Aspen HYSYS** and VMGSim, **AutoCAD**, ChemOffice, SigmaPlot
- Advanced user of **MS Office** and Corel Draw
- Highly proficient in spoken and written **English and Russian**

COMMUNICATION

- Drafted and revised research manuscripts in a team effort. Prepared and published a book chapter covering mathematical methods for optimization of catalytic reactors
- Prepared and delivered 5 oral and 1 poster presentations for academic and engineering audiences, including talks at AIChE 2016 and CSChE 2016
- Wrote several technical reports and presented results to plant engineers and management
- Experienced in communicating effectively and professionally with individuals from a wide variety of disciplines and career levels
- Maintained confidentiality, and worked with proprietary information and documentation such as PFDs, P&ID, equipment drafts, etc.