Control System for Ammonia Synthesis Column

Matei Vinatoru

Automation Department, University of Craiova,
Al. I. Cuza Street, No. 13, 1100-Craiova, ROMANIA,
*(e-mail: vinatoru@automation.ucv.ro)*

Abstract: The paper presents the possibilities of simulation of steady and dynamic regimes for ammonia synthesis columns. We present the possibilities of study of the dynamic regimes for automatic control of the temperature in catalyst layers and propose an advanced control structure using the fresh gas flows between catalyst layers as commands. We also present the possibilities of optimization of the column steady states to obtain a higher conversion factor using the control of gas flows between the catalyst layers. This optimization algorithm is part of the main advanced control program for the synthesis column.

Keywords: Advanced control system, modeling, simulation, ammonia plant synthesis.

1. INTRODUCTION

Ammonia synthesis is the first stage in the manufacturing of nitrous chemical products (fertilizers, plastics, explosives, etc.). The direct synthesis process, from basic gases (hydrogen and nitrogen) needs a theoretical and experimental study of the synthesis installation, in order to determine the optimum working regimes. In ammonia production unit, the synthesis loop is located after the synthesis gas production and purification units. Ammonia synthesis process takes place at high pressure and hence high power multi cycle compressors are used to supply the required pressure.

The synthesis of ammonia using a form of magnetite iron oxide, as the catalyst, is developed proceeding from chemical reaction (Haber process):

$$N_2(g) + 3 H_2(g) \quad NH_3(g) \quad (\Delta H = - 92.4 kJ.mol^{-1}) \quad (1)$$
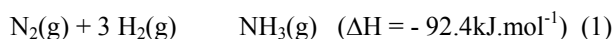
This is done at 150 - 300 bar and between 300 and 550 ^{o}C passing the gases over four layers of catalyst, with cooling between each pass, to maintain a reasonable equilibrium constant. The cooling is obtained by the injection of cool flows of synthesis gas in the quench zone. (see figure 1). On each pass only about 15% conversion occurs, but any unreacted gases are recycled, so that eventually an overall conversion of 98% can be achieved.

There are two opposing considerations in this synthesis: the position of equilibrium and the rate of reaction. At the normal temperature the reaction is slow and the best solution is to raise the temperature. This may increase the rate of reaction but since the reaction is exothermic it also has the effect of favouring the reverse reaction that decomposes the ammonia resulted in direct reaction. In these conditions, in the industrial synthesis of ammonia, the ammonia reaction is stable at the equilibrium point, given by equilibrium constant k_{eq}:

$$k_{eq} = p_{NH_3}^2 \big/ (p_{N_2} . p_{H_2}^3) = f(T, p) \quad (2)$$

were p_i partial pressures of components and it is function of temperature and pressure (see annexe B).

The temperature around 400°C and the pressure around 200 bar ensure a profitable yield that gives a single pass yield of around 15%.

Another way to increase the yield of reaction would be to remove the ammonia gas from the system but in practice gaseous ammonia is removed from the mixture of gases (NH_3, H_2, N_2, CH_4, Ar) leaving the reaction column. The hot gases are cooled enough for the ammonia to condense and be removed as liquid. Unreacted hydrogen and nitrogen gases are then returned to the reaction column to undergo further reaction.

The optimum working regimes must be determined in the following conditions:

1. The direct synthesis reaction $N_2 + 3 H_2 \quad NH_3$ is a reversible exothermic reaction which must take place at equilibrium to get a maximum conversion rate.

2. The conversion rate depends of a series of technological factors, the most important being: temperature (the temperature increase leads to ammonia decomposition, thus leading to conversion rate decrease), catalyst activity (which is decreasing in time because of catalyst exhausting) and pressure. The maximum ammonia concentration that can be obtained is between 14% and 22% and depends of the pressure and the temperature.

3. The synthesis columns are built with fixed catalyst layers and there is no possibility to control the temperature inside the catalyst layer. To compensate this inconvenience, the columns are built with multiple catalyst layers (Kellog process), offering the possibility of introduction of cold gas between the layers in order to

reduce the temperature and ammonia concentration at the input into the next layer, thus increasing the quantity of produced ammonia and the conversion rate.

4. The catalyst is spent non-uniformly, starting with the first layer. Controlling the injection flows on each layer leads to efficient use of the catalyst, increasing the conversion rate on ending layers while the beginning layers are exhausted, thus increasing the quantity of produced ammonia and the conversion rate.

5. The real catalyst activity can be different from the manufacturer specifications. Using optimizing software based on real process measurements, the real catalyst activity value can be determined and further used for control.

Therefore, this paper tries to solve the following problems:

- The development of simplified models and programs for the column working regimes:

- The modelling of the steady states considering the variations of the concentration and temperature along the catalyst layers (the variation against the spatial coordinate).

- The development of optimization procedures for the steady states, using as optimization criteria the maximum final conversion rate, and the calculation of optimum cold gas flows to be injected between layers.

- The modelling of the dynamic regimes considering the catalyst layers as a lumped parameter system and developing real time control software for the control of temperatures and cooling flows.

- The development of fault detection and correction algorithms (actuator blocking, malfunctioning of temperature sensors) and control algorithms in fault conditions for the column during the repair periods.

2. COLUMN MODELING AND SIMULATION

2.1 Industrial considerations

Ammonia is the primary feedstock for the nitrogenous fertilizer industry. Many of ammonia technology companies (for ex. Kellogg Brown & Root, Romanian Chemical Industry) develop strong research activities in the direction of engineering, construction, training, control, and operating and maintenance services.

One of industrial procedures to obtain ammonia (NH_3) from components, nitrogen (N_2) and hydrogen (H_2) takes place at medium pressure (p = 150 bar) in a multi-layer synthesis column (usually four layers). The column structure is presented in figure 1.

The main feed of the synthesis column consist of flow F_1, at a temperature T_0 of 290-300 degree Celsius, that is preheated to 400 degree Celsius in the heat exchanger located at the column entrance. The synthesis reaction that takes place in the catalyst layers is highly exothermic. Thus, through flows F_2, F_3, and F_4 introduced between catalyst layers at a temperature T_0, we get the following:
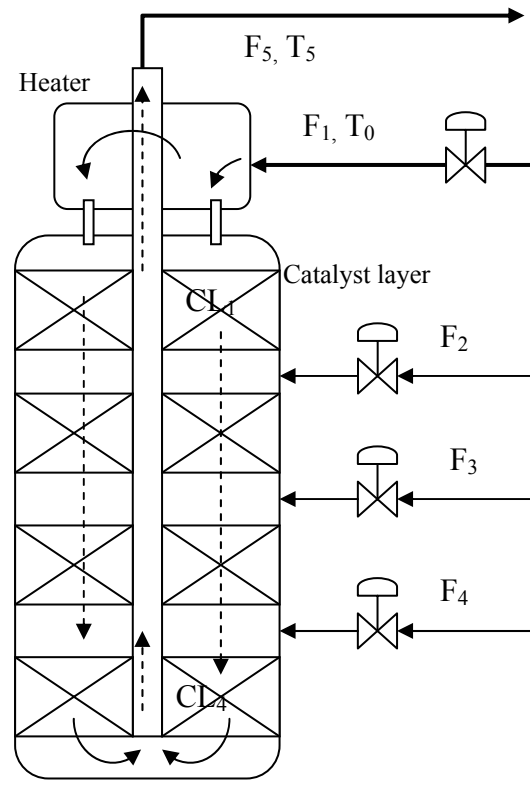

Fig. 1. Synthesis column with four catalyst layers

- direct gas cooling between catalyst layers in order to maintain the optimum reaction parameters in the new layer;

- reduction of the ammonia concentration in the gas mixture (H_2, N_2, CH_4, NH_3) below the equilibrium value, in order to allow the ammonia production increase per production unit.

This paper tries to develop a control strategy to realize a maximum conversion of reactants that can be obtained for a given status and functional parameters at the reactor entrance, and for fixed geometry of catalyst systems. During operation perturbing factors can appear which necessitate the use of advanced control structures and appropriate control algorithms.

2.2 Dynamical model

The processes inside of catalyst layers correspond to a distributed parameter process. The process parameters (temperature, concentration, pressure) are achieved at the end of each layer as industrial data but are not usually available along the length of the layer. In this case, through modelling of the synthesis, reactor temperature, concentration, and pressure profiles can be obtained.

The following assumptions have been made for this modelling:

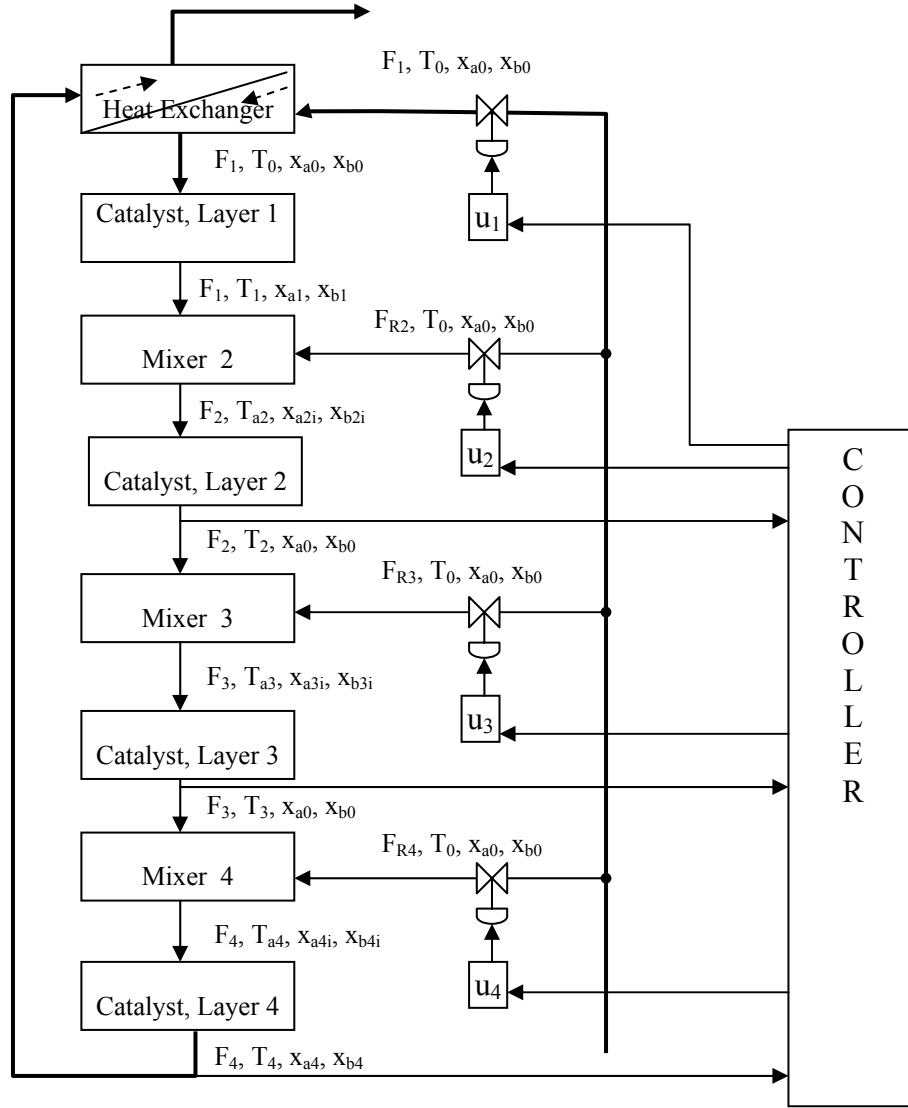- Density of catalyst is constant;

Fig. 2. Block Diagram

- Concentration and temperature on catalyst surface and bulk of gas are equal;

- The effects of penetration resistance in catalyst and catalyst inside concentration (activities) have been incorporated in the equations by a coefficient;

- One-dimensional Cartesian coordinate has been considerate along with the bulk flow.

From the analysis of the technological flow, we can obtain the block diagram of the ammonia synthesis column that is shown in figure 2.

In order to obtain a simpler dynamic model for the synthesis column, the column was decomposed in eight functional blocks. For each block we can write the mass balance equations for nitrogen and hydrogen and the thermal balance equation for the gas mix. We are taking into consideration the reaction speeds that depend of the working temperature and pressure in each layer zone. The coefficients appearing in the equations can be determined partly using the relations from literature and partly from

measurements in the real installations. Finally, after coefficient correction and model validation, we obtain the following model for the synthesis column:

a) *Heat Exchanger:*

$$\frac{dT_{a1}}{dt} = \frac{F_j}{1000}(c_{p0}T_0 - c_a T_{a1}) + 5.0392(T_4 - T_{a1})$$

(3)

b) *Catalyst layer j*

$$\frac{dx_{aj}}{dt} = \frac{F_j}{1000}c_j(x_{a0} - x_{aj}) + \frac{F_{Rj}}{1000}c_j(x_{a0} - x_{aj}) +$$
$$+ c_{Rj}K_{Tj}(T_j)V_{Rj}(x_{aj},x_{bj})$$

(4)

$$\frac{dx_{bj}}{dt} = \frac{F_j}{1000}c_j(x_{b0} - x_{bj}) + \frac{F_{Rj}}{1000}c_j(x_{b0} - x_{bj}) +$$
$$+ c_{Rj}K_{Tj}(T_j)V_{Rj}(x_{aj},x_{bj})$$

(5)

$$\frac{dT_j}{dt} = \frac{F_j}{1000}(c_{aj}T_{aj} - c_{pj}T_j) -$$
$$- H_{Rj}K_{Tj}(T_j)V_{Rj}(x_{aj},x_{bj})$$

(6)

c) Mixer j

$$\frac{dT_{aj}}{dt} = \frac{F_{j-1}}{1000}(c_{pj-1}T_{pj-1} - c_{pj}T_j) +$$
$$+ \frac{F_{Rj}}{1000}(c_{p0}T_0 - c_{pj}T_j) \tag{7}$$

$$V_{Rj} = 0.9x_{aj}\left[\frac{x_{bj}^3}{(0.60648 - x_{aj} - x_{bj})^2}\right]^{0.521} -$$
$$\left[\frac{(0.60648 - x_{aj} - x_{bj})^2}{x_{bj}^3}\right]^{0.479} \tag{8}$$

$$K_{Tj} = \exp\left(27.751 - \frac{25107.7}{T_j}\right) \tag{9}$$

were:

- $j = \overline{1,4}$ $F_{R1} = 0$, $F_1 = 18860$ Kmol/h, $F_j = F_{j-1} + F_{Rj}$;
- c_j, c_{p0}, c_{p1}, c_{pj} are thermal and mass coefficients,
- T_j (j=1…4) are temperatures in the catalyst layer j
- T_{aj} (j=1..4) are temperatures at the output of the mixer j

- x_{aj}, x_{bj} are the concentrations of the nitrogen and hydrogen on the layer j

$F_2 = F_1 + F_{R2}$; $F_3 = F_1 + F_{R1} + F_{R2}$; $F_4 = F_1 + F_{R1} + F_{R2} + F_{R3}$;

The coefficient values are presented in Annex, table 1. The mathematical model of the synthesis column given by (3) to (9) was implemented in Matlab in order to study the column operation in dynamic regime, to determine the sensitivity of the commands u_1 to u_4 (see figure 2) reported to column parameters and the allowed ranges for commands and to determine the temperature ranges in the column for temperature sensors design.

Because of the high cost of the gas concentration sensors, temperature sensors mounted inside the catalyst layers and mixing areas are used to provide feedback for the control algorithms.

3 OPTIMIZATION PROCEDURES FOR THE MAXIMUM FINAL CONVERSION RATE

In order to obtain maximum conversion rate of nitrogen and hydrogen into ammonia, we must determine the optimum cooling flows between the catalyst layers and working temperatures in the column. Advanced control algorithms determine these parameters periodically or on demand, using an optimization algorithm.

The optimization algorithm is based on the following hypotheses:

-The equivalent reaction for each layer is considered adiabatic;

-The catalytic reactions are taking place in quasi-homogenous layers;

-The gas cooling is considered instantaneous compared with the mass and heat transfer inside the catalyst layer;

-The gas flow through the catalyst layer can be approximated by a travelling model;

-Pressure losses on catalyst layers are negligible;

In steady state, for each catalyst layer we can define the mathematical model of the process:

a) Conversion rate

$$\frac{dx_{aj}}{dz} = \frac{S}{F_{MN0}}V_{Raj} \tag{10}$$

b) Heat accumulation inside the gas mix and catalyst

$$\frac{dT_j}{dz} = -\frac{S}{F_M c_p}(-\Delta H_{Ra})V_{Raj} \tag{11}$$

where: x_{aj} = conversion rate on layer j, T_j = temperature on layer j, F_{MN0} = nitrogen molar flow at the reactor entrance, c_p = molar specific heat of the synthesis gas, V_{Raj} = reaction speed, ΔH_{Ra}=reaction enthalpy (depends on T) (see Appendix A).

The reaction speed can be represented as a function of catalyst used and reactants' (NH$_3$, N$_2$, H$_2$) concentrations in real and equilibrium conditions (Tempkin-Pijev model).

$$V_{Raj} = \frac{K_{tj}(T)}{\sqrt{p}}\left[\frac{y_{NH_3}^{*2}}{y_{H_2}^{*3}y_{N_2}^{*}}\frac{y_{H_2}^{1.5}y_{N_2}}{y_{NH_3}} - \frac{y_{NH_3}}{y_{H_2}^{1.5}y_{N_2}}\right] \tag{12}$$

were y_i^* is the equilibrium concentration and y_i is reaction resulted concentration, p is the work pressure in the layers and $K_{tj}(T)$ is rate constant for reaction offered by Dyson & Simon in 1968 as function of temperature T [Woinaroschy 1990]:

$$K_{tj}(T) = 10.43.\exp[(1/273 - 1/T).22730].$$

Equilibrium concentrations and constants can be represented as a function of equilibrium conversion rate x_e and fugacity coefficients for N$_2$, H$_2$ and NH$_3$.

Eventually we obtain an algebraic equation that gives us the equilibrium conversion rate:

$$a_2 x_e^2 - 2a_1 x_e + a_0 = 0 \tag{13}$$

were

$$a_2 = 5.196.K_{eq} + 4$$
$$a_1 = 5.196K_{eq} + 4 - (F_i + F_{Ri})(x_{CH4} + x_{Ar}).F_1$$
$$a_0 = 5.196K_{eq} - \frac{x_{NH3}^0(F_i + F_{Ri})}{F_1}.$$
$$\cdot\left[4 + \frac{F_i - F_{Ri-1}}{F_1}\left(x_{NH3}^0 + x_{CH4}^0 + x_{Ar}^0\right)\right]$$

and F_i, F_{Ri} , x_i corresponds to figure 2.

The real solutions of the equation represent the maximum possible value for the conversion rate. At the entrance in the new catalyst layer we determine the conversion rate:
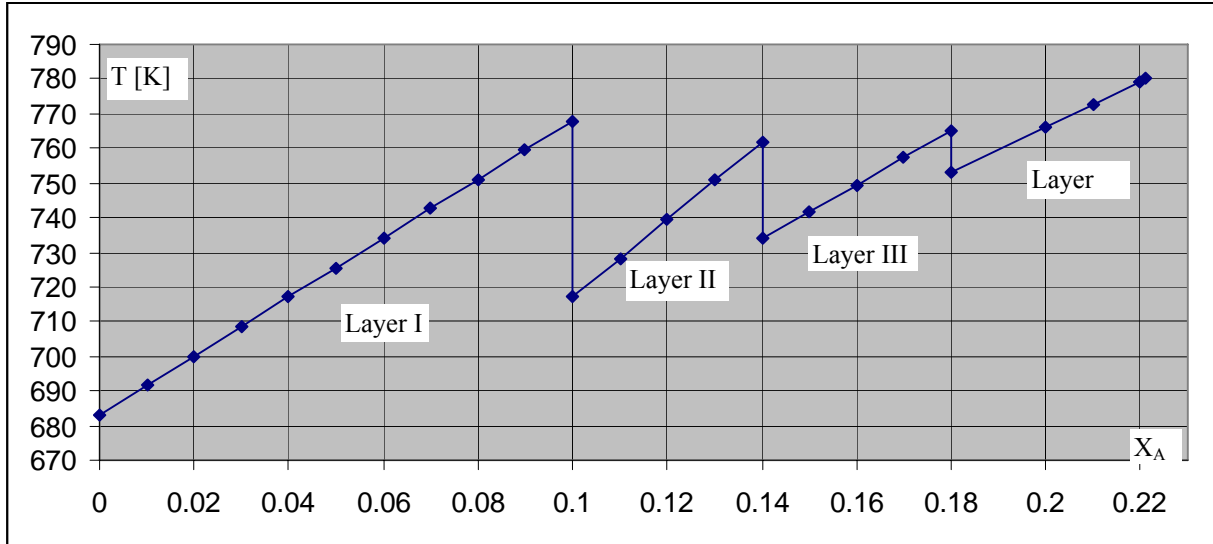
Fig. 3. Evolution of conversion rate and temperature for each layer

$$x_j = \frac{x_{ej-1}F_{10}}{F_{10} + \sum\limits_{i=}^{j} F_{Ri}} \tag{14}$$

and temperature

$$T_j = \frac{F_m c_{pm} T_{ej-1} + F_{Ra} c_{pj} T_1}{(F_m + F_{Ra})c_p} \tag{15}$$

Results taken from simulations are compared with industrial data. Input conditions are as below:

Reactor input pressure 150 bar

Reactor input temperature 683 K

Input flow rate to reactor 180.000 Kg/h

Input composition:
$$x_{N2}^0 = 0.211, \quad x_{H2}^0 = 0.633, \quad x_{NH3}^0 = 0.0211,$$

$$x_{CH4}^0 = 0.1, \quad x_{Ar}^0 = 0.03,$$

Relations (10-15) can be integrated using initial conditions x=0 and $T_{i0}=T_1$ and we can obtain the optimum flow F_i and temperatures at the entrance of each layer: F_{R2}=3000Kmol/h, F_{R3}=1900 Kmol/h, F_{R4}=600 Kmol/h, T_2=717 K, T_3=734 K, T_4=753 K and the final conversion is X_A = 0.221. The 4th order Runge Kutta approach was used to solve the above set of equations. As this set of equations is stiff, pressure drop equations is first taken out of the set and the new set with two equations is solved using Runge Kutta numerical method. At each stage of the numerical solutions, pressure drop must be calculated by means of the temperature and concentrations derived from that stage and in this case the temperature, pressure and conversion rate are determined.

To calculate the pressure drop, inside layers, Ergun equation can be applied [Zardi, 1992]. In practice, pressure drop is more than that shown by modelling as in the related simulation the catalyst particles are assumed to be spherical. Industrial catalyst doesn't have a regular shape which increases the pressure drop. In this case we consider a linear variation of pressure inside layers, calculate with pressure data from input and output of the industrial synthesis column.

In figure 3 is presented the dependence between the conversion rate and temperature for each layer. The temperature changes along the layers. In first layer, as the ammonia concentration is low, the reaction rate is very high and the temperature increases along the layer while approaching equilibrium at its end (the slope of the curve is reduced along the layer). After first layer, gas is cooled down in internal heat exchanger causing that to get far from equilibrium. As it is observed in the figure, the gas approaches equilibrium at the end of third layer and the temperature change is low. As previously mentioned, one of the capabilities of the developed software is investigation of changes in the unit outputs. Analysis of these results, can lead us to find bottlenecks and high production ways, etc

Figure 4 illustrate the changes of N_2 conversion rate along the layers. It is observed that changes along the first layer are more severe than those of the second, third and four ones because of the lower reaction product content in the feed of these layers.

4 ADVANCED CONTROL OF SYNTHESIS COLUMNS IN FAULT CONDITIONS

In figure 5 is presented the block diagram of the advanced control system for the synthesis column. The system provides the temperature and cooling flow control, based on optimum values provided by the optimization block.

This strategy uses the flows F_1 to F_4 to get a maximum conversion rate and a maximum production for normal working conditions. Also, these flows can be used in the case of a temporary fault of the main feed (actuator fault for the flow F_1) or in the case of catalyst exhaustion for the first or second layer.
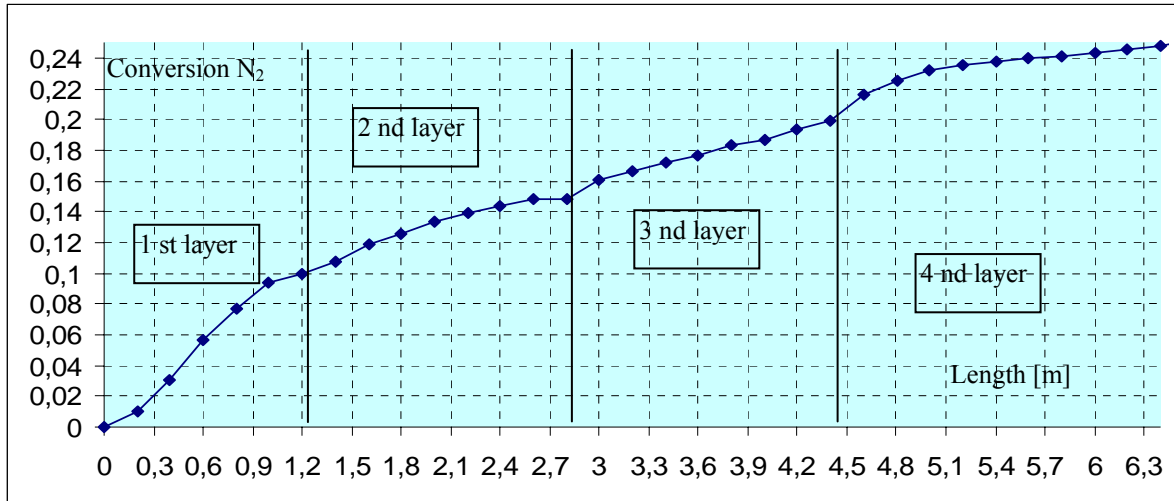
Fig. 4 . The changes of N_2 conversion rate along the layers

For advanced control, the conventional control of the ammonia synthesis column at the Kellogg ammonia plant from Craiova was replaced with numeric control (DCS and PLS), using a hierarchical distributed control structure. Beside the standard software, new software was developed to monitor and optimize the synthesis process.

The program structure for advanced control of the synthesis column is presented in figure 6.

Periodically, during operation, the optimal procedure is called to compute the optimal flows F_1 to F_4 and optimal temperatures at the entrance and exit of every layer, using the current data from the process (temperatures, pressures, gas composition).

For the first stage, we ran a computer simulation of the system, using mathematical models, based on termochemical kinetics and data for the actual catalyst

used in the process.

The results were very close to the real data obtained from the process. In figures 3 and 4 are represented the diagram of the temperatures and concentrations for each catalyst layer. The program allowed the simulation of different fault conditions such as actuators blocking and allowed the development of control strategies for the synthesis column using the other available flows.

The conversion rate can be maintained, in certain conditions, close to the normal but the ammonia production decreases with 25%.

The operating logs for some ammonia columns from the ammonia plants have revealed a series of faults that can appear in the equipment or in the control structure:

-Blocking or hysteresis operation of actuators for layer flows F_1, F_2, F_3 and F_4.

-Improper preheated synthesis gas or improper pressure control in the compressor zone that can lead to important changes in hot gas temperature T_i or flow F_i.

-Changes of the heat transfer coefficients caused by build up inside or outside the super heater's pipes and coils. It is necessary to highlight the action channels for these possible faults and the measurable outputs of the process that are directly and faster modified by these perturbations. Using the equations (3 - 7) we can develop the block diagram presented in figure 6. We can define the pairs that represent the direct channels fault-perturbed output: (F_2 - T_2, F_3 - T_3) and the remaining available pair (T_i - T_1), although T_i can also modify simultaneously T_2 and T_3. The perturbations in the synthesis system (T_i and F_i) can also modify T_1. Accordingly we can define the error vector DE as a matrix function of fault vector DE.
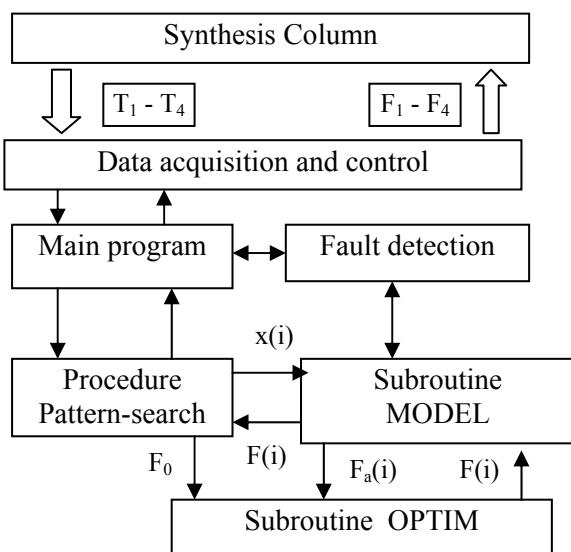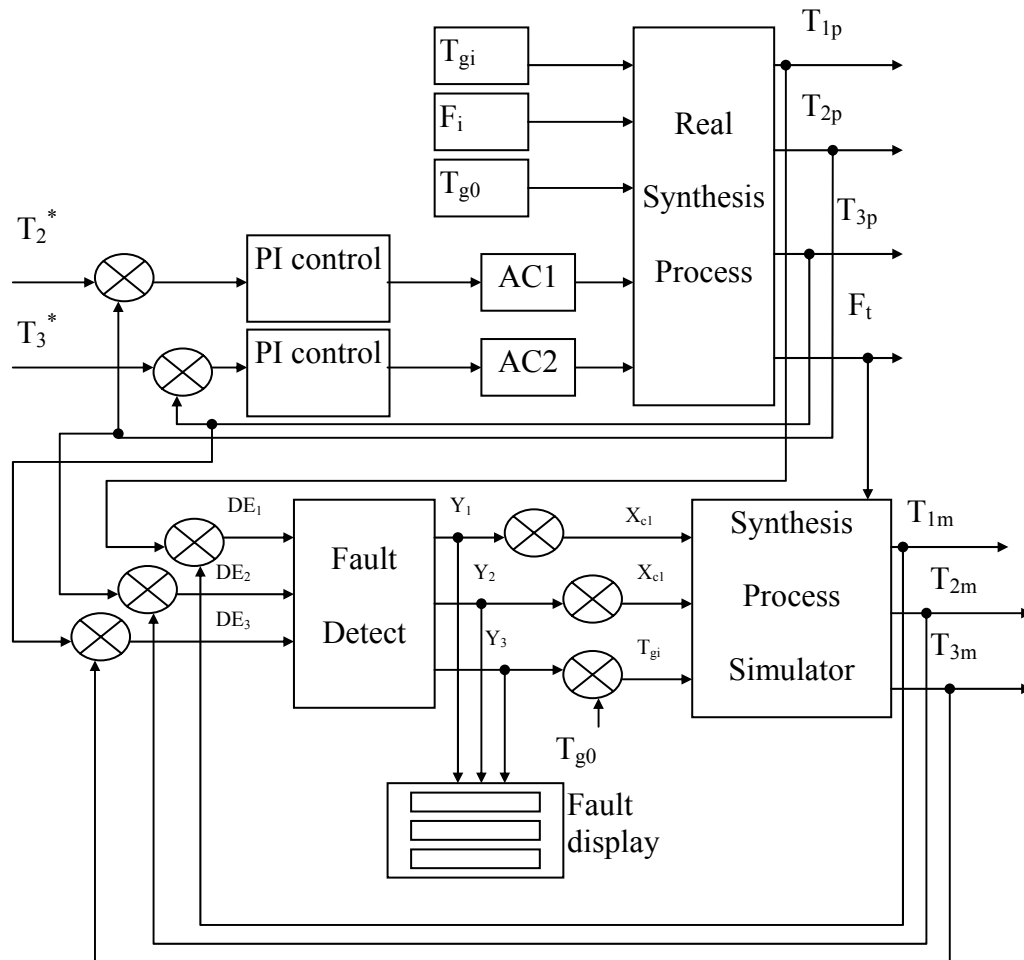

Fig. 5. Control structure

Fig. 6. Fault detection and isolation bloc diagram

$$DE = \begin{bmatrix} T_{2p} - T_{2m} \\ T_{3p} - T_{3m} \\ T_{1p} - T_{1m} \end{bmatrix} = F\left(\begin{bmatrix} F_2 \\ F_3 \\ T_i \end{bmatrix} \right) \qquad (14)$$

Applying the analytical method principles presented in [Vinatoru, 1997, 1998] we will obtain the block diagram, presented in figure 6 that was verified through simulation.

5 CONCLUSIONS

The simulation of ammonia synthesis process under basic operating conditions agrees satisfactorily with design data. Simulation under different conditions provides a better understanding of effects of process variables on ammonia synthesis operations, in normal or fault conditions.

The program allows the operators from the control room to permanently evaluate the working conditions and compare them with the optimal values.

- It allows the permanent control of process parameters.

- It allows the simple adaptation to the real optimal working conditions.

REFERENCES

Crove, C. (1971) *Chemical Plant Simulation*, Prentice-Hall, London.

Dashti, A., Khorsand1, K., Marvast, M, A., Kakavand, M., (2006), Modelling and simulation of ammonia synthesis reactor, *Petroleum & Coal* 48 (2), 15-23.

Gillespie, L., J., J. A. Beattie, (1930), Ammonia Synthesis, Phys. Rev., Vol. 36, pp. 734, 1930

Elnashaie S.S.E.H., S.S. Elshishini, (1993) "Modelling, Simulation, and Optimization of Industrial Fixed Bed Catalytic Reactors", G&B Science.

Iancu, E., M. Vinatoru, *Fault Detection and Identification in Dynamic Systems* , Craiova, Sitech, Romania, 1999.

.Isermann, R, (1997) Supervision, fault detection and fault diagnosis methods. *An introduction, Control Engineering Practice,* 5(5), 1997, pp. 639 – 652.

Jennings, J. R. *Catalytic Ammonia Synthesis: Fundamentals and Practice*, Plenum Press, New York,.

Vinatoru, M., (2001) *Automatic Control of Industrial Processes*, Ed. Universitaria, Craiova.

Vinatoru, M., E. Iancu, C. Vinatoru, (1997) Robust control for actuator failures, *Proceedings of 2nd IFAC Symposium ROCOND'97*, Budapest, pp. 537 - 542.

Vinatoru, M., E. Iancu, C. Vinatoru, R.J.Patton, J. Chen, (1998) Fault Isolation Using Inverse Sensitivity

Analysis, International *Conference on Control'98,* University of Wales, Swansea, England, vol. 2, pp. 964-968.

Woinaroschy A., M. Mihai, R. Isopescu, (1990) *Process Optimisation from Chemical Plant*, Thenica Editure, Bucharest.

Zardi, F., D. Bonvin, (1992), Modelling, Simulation and Validation for an Axial- Radial Ammonia Synthesis , *Chemical Engineering Science*., Vol. 47, No. 9-11 , pp. 2523.

Appendix A.

Table 1. Equation constants

Const	Layer I	Layer II	Layer III	Layer IV
c_i	5.504	3.4673	2.01	0.5225
c_{Ri}	1	0.514	0.635	0.12793
c_{aj}	5.4763	3.40831	1.992	0.5225
c_{pi}	5.5048	3.4621	2.01	0.5225
c_{p0}	0.2133	0.21229	0.11239	0.11229

ΔH_{Ra}- reaction enthalpy [Woinaroschy, 1990]:
$$\Delta H_{Ra}= 9157.0 + (0.54526 + 840.6/T + 4.59734/T^3).p + 5.3465 .T + 2.2525*10^{-4} T^2 -1.6917*10^{-6} T^3$$

Appendix B: Equilibrium constant

$$K_{eq} = \frac{x^*_{NH3}}{\sqrt{x^*_{N2}}\sqrt{\left(x^*_{H2}\right)^3}} = p\frac{K_a}{K_\gamma}$$

In 1930, Gillespie and Beattie have developed the following equation to calculate the equilibrium constant [Gillespie, 1930].

$$\lg K_a = -2.6911 \lg T - 5.5193.10^{-3}.T + 1.8488.10^{-7}.T^2 + 2001.6/T+2.6899$$

$$K_{eq} = \frac{\gamma_{NH3}}{\sqrt{\gamma_{N2}}\sqrt{\left(\gamma_{H2}\right)^3}} = p\frac{K_a}{K_\gamma}$$

were γ is the fugacity coefficient of the reaction product and reactants and p is the total pressure in the layer j [Woinaroschy, 1990]

$$\gamma_{N_2} = 0.9431737 + 0.3102\cdot10^{-2}T + 0.2959\cdot10^{-2}p - 0.27073\cdot10^{-6}T^2 + 0.47752\cdot10^{-6}p^2$$

$$\gamma_{NH_3} = 0.1438996 + 0.20285\cdot10^{-2}T + 0.44877\cdot10^{-2}p - 0.11429\cdot10^{-5}T^2 + 0.2761216\cdot10^{-6}p^2$$

$$\gamma_{H_2} = \exp\left\{\begin{array}{l} p\cdot\exp\left(-3.8402T^{0.125} + 0.541\right)- \\ -p^2\exp\left(-0.136T^{0.5} -15.98\right) \\ +300[\exp\left(-0.0119T -5.941\right)* \\ *[\exp(-300p)-1] \end{array}\right\}$$