Optimization of an auto-thermal ammonia synthesis reactor using cyclic coordinate method

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Abstract. The ammonia synthesis system is an important chemical process used in the manufacture of fertilizers, chemicals, explosives, fibers, plastics, refrigeration. In the literature, many works approaching the modeling, simulation and optimization of an auto-thermal ammonia synthesis reactor can be found. However, they just focus on the optimization of the reactor length while keeping the others parameters constant. In this study, the other parameters are also considered in the optimization problem such as the temperature of feed gas enters the catalyst zone, the initial nitrogen proportion. The optimal problem requires the maximization of an objective function which is multivariable function and subject to a number of equality constraints involving the solution of coupled differential equations and also inequality constraint. The cyclic coordinate search was applied to solve the multivariable-optimization problem. In each coordinate, the golden section method was applied to find the maximum value. The inequality constraints were treated using penalty method. The coupled differential equations system was solved using Runge-Kutta 4th order method. The results obtained from this study are also compared to the results from the literature.

1. Introduction

Ammonia is one of the most important synthetic chemical product in the world. Most of the commercially produced ammonia is used in fertilizers with the remainder used in a variety of applications such as plastics, synthetic fibers and resins, pharmaceuticals, explosives, papers and refrigeration [1]. Therefore, modelling and optimization of ammonia synthesis have received a considerable attention by industries and researcher. Most of the world consumption is manufactured from the elements nitrogen and hydrogen in a catalytic process originally developed by Haber and Bosch using a promoted iron catalyst as follows:

\[ N_2 + 3H_2 \rightleftharpoons 2NH_3 \]  \hspace{1cm} (1)

The reaction is reversible and exothermic with considerable release of heat. Therefore, the reaction is usually carried out in an auto-thermal synthesis reactor, which utilizes the heat of reaction to pre-heat the feed gas and maintain the appropriate temperature inside. The production of ammonia depends on several factors such as the reactor length, temperature of feed gas, temperature of the reacted gas mixture at the exit of the reactor, and the mass flow rate of nitrogen. The optimization problem consists of maximizing the economic return from the process. There are many study discussing the modelling,
simulation, and optimization of an auto-thermal ammonia synthesis reactor. Some of them can be mentioned here as in Babu and Angira [2], Babu et al. [3], Carvalho et al. [4], Edgar et al. [5], Ksasy et al. [6], Murase et al. [7], Upreti and Deb [8], Yusup et al. [9]. However, in the studies of Edgar et al. [5], Murase et al. [7], the model used has some uncorrected points and have been modified in Upreti and Deb [8]. Furthermore, the studies mainly focus on the optimization of reactor length corresponding to a particular reactor top temperature, usually of 694 K [3, 4], or in only several temperatures [6].

In this study, not only the reactor length but also the reactor top temperature is included in the optimization variables for finding the maximum profit of the process. The coupled differential equations which simulate the synthesis reactor are solved using Runge-Kutta 4th order method. Cyclic coordinate search method was applied for the multivariate optimization problem. In each coordinate axis search, the problem becomes single variable optimization and the golden section search was employed to find the maximum of the profit. The box-constraints of the parameters were guaranteed by adding the penalty to the objective function when any of the limits is violated. The results from the study are also compared to the other reports found in literature.

2. Problem formulation

The problem formulation in this work is similar to the model in Murase et al. [7] and includes the modifications mentioned in Babu and Angira [2], Upreti and Deb [8]. The heat released by the reaction is used to heat the incoming gas mixture in counter current flow. The production of ammonia depends on the temperature of feed gas at the entrance of the reaction zone (top temperature), the partial pressures of the reactants (nitrogen and hydrogen), and the reactor length. The optimal design problem aims to obtain the optimal parameters yielding maximum economic return from the reactor operation.

2.1. Objective function

The objective function for the reactor optimization is the profit of the process based on the difference between the value of the product gas (heating value and the ammonia value) and the value of feed gas (as a source of heat only) less the amortization of reactor capital costs. Other operating cost are neglected.

\[
F = 1.3356 \times 10^7 - 1.708 \times 10^4 N_{N_2} + 704.09(T_g - T_f) - 699.27(T_f - T_g) - \left(3.4566 \times 10^7 + 1.9837 \times 10^8 x\right)^{\frac{1}{3}} \tag{2}
\]

2.2. Equality constraints

The model of ammonia reactor is obtained considering the energy balance for feed gas and reacting gas, and the mass balance for nitrogen, respectively.

\[
\frac{dT_f}{dx} = \frac{US_f}{WC_{pf}}(T_g - T_f) \tag{3}
\]

\[
\frac{dT_f}{dx} = \frac{US_f}{WC_{pf}}(T_g - T_f) + \frac{(-\Delta H)S_f}{WC_{pf}} \left(-\frac{dN_{N_2}}{dx}\right) \tag{4}
\]

\[
\frac{dN_{N_2}}{dx} = -f_k \left(k_1 \frac{P_{N_2}P_{H_2}^{1.5}}{P_{N_2}P_{H_2}^{1.5}} - k_2 \frac{P_{N_2}P_{H_2}^{1.5}}{P_{N_2}P_{H_2}^{1.5}} \right) \tag{5}
\]

in which

\[
k_1 = 1.78954 \times 10^4 \exp\left(-\frac{20800}{RT_g}\right) \tag{6}
\]

\[
k_2 = 2.5714 \times 10^{16} \exp\left(-\frac{47400}{RT_g}\right) \tag{7}
\]

\[
P_{N_2} = \frac{286 N_{N_2}}{2.598N_{N_2} + 2N_f} \tag{8}
\]
$$p_{H_2} = 3p_{N_2}$$

$$p_{NH_3} = \frac{286(2.23N^0_{N_2} - 2N_{N_2})}{2.598N^0_N + 2N_{N_2}}$$

The notations $T_f^0, T_g^0$, and $N_{N_2}^0$ denote the initial value at $x=0$ for $T_f, T_g$, and $N_{N_2}$, respectively. The initial values are given by

$$T_f^0 = T_g^0 = T_0, \quad N_{N_2}^0 = 701.2 \text{ kmol/hm}^2$$

2.3. Box constraints

As usual in industry, the following physical restrictions are imposed over the variables:

$$0 < x \leq 10, \quad 400 \leq T_r \leq 800, \quad 0 \leq N_{N_2} \leq 3220$$

From the system model, it can be obtained that the length of the reactor and the top temperature can be chosen as the independent variables. The remaining variables ($T_f, T_g$, and $N_{N_2}$) can be calculated from the three differential equations. From that, the objective function is estimated and is considered as a function of two variables $T_0$ and $x$. From the constraints, the variable $T_0$ is also set to be within 400 and 800.

The optimal design problem is summarized as follows

$$\max F(x, T_0)$$

$$\begin{align*}
\frac{dT_f}{dx} &= \frac{US_f}{WC_{pf}}(T_g - T_f) \\
\frac{dT_g}{dx} &= -\frac{US_g}{WC_{pg}}(T_g - T_f) + \left(\frac{\Delta H}{WC_{pg}}\right) \left(\frac{dN_2}{dx}\right) \\
\frac{dN_2}{dx} &= f\left(k_1 \frac{p_{N_2}p_{H_2}^{1.5}}{p_{NH_3}} - k_2 \frac{p_{SH_3}p_{H_2}^{1.5}}{p_{H_1}^{1.5}}\right)
\end{align*}$$

3. Optimization strategy

The procedure to solve problem (13) consists of obtaining approximate solutions of differential equation system (3), (4) and (5), with initial conditions (11) through the fourth-order Runge–Kutta method. The initial condition is clearly defined when the top temperature ($T_0$), which is also a variable, is assigned. The interval of integration is defined when the reactor length is assigned. From these computed values, the objective function is evaluated and the procedure above is repeated until an optimal solution is found. Therefore, the problem can be considered as two-variable optimization and the simple cyclic coordinate search can be employed. In order to guaranty the constraints, the objective function is forced to assume an undesired value whenever any of variable limits is violated during the optimization process. Such approach consists of defining a penalty or barrier to the objective function when any of the limits is violated.

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\frac{dN_2}{dx} &= f\left(k_1 \frac{p_{N_2}p_{H_2}^{1.5}}{p_{NH_3}} - k_2 \frac{p_{SH_3}p_{H_2}^{1.5}}{p_{H_1}^{1.5}}\right)
\end{align*}$$

3.1. Cyclic coordinate search

Often in the solution of multivariable optimization problems it is desired to be done with a gradient-free algorithm. This may be the case when gradient evaluations are difficult, or in fact gradients of the
underlying optimization method do not exist. Such a method that offers this feature is the method of the cyclic coordinate search, the simplest method for nonlinear optimization [10].

The minimization problem considered is: optimize \( f(x) \)

The method in its basic form uses the coordinate axes as the search directions. Therefore, along each search direction \( i = 1 : n \), the corresponding variable \( x_i \) is changed only, with all remaining variables being kept constant to their previous values.

The optimization is carried out in order over all variables with indices \( 1, \ldots, n \) at each iteration of the algorithm. The task is repeated until the convergence condition satisfied, such as no significant improvement after one cycle.

Step 1. Initialization

Select a tolerance \( \epsilon > 0 \), to be used in the termination criterion. Select an initial point \( x(0) \) and initialize by setting \( z(1) \leftarrow x(0) \). Set \( k = 0 \) and \( i = 1 \), where \( k \) indicates the number of iterations, \( i \) is the pointer variable for the direction.

Step 2. Main iteration

Search the optimal solution \( f(z^*) = \text{opt} f(x) \), which is the single-variable optimization of variable \( x_i \).

Update \( z(i+1) = z^* \).

If \( j < n \), then increase \( i \) to \( i + 1 \) and repeat step 2. Otherwise, if \( j = n \), then go to step 3.

Step 3. Termination check

Set \( x(k+1) = z(n) \). If the termination criterion is satisfied, for example \( \text{abs}(x(k+1) - x(k)) < \epsilon \), then stop.

Else, set \( z(1) = x(k+1) \). Increase \( k \) to \( k + 1 \), set \( i = 1 \) and repeat step 2.

3.2. Barrier method for constrained optimization

In barrier or penalty method, a constrained optimization problem is replaced by an unconstrained problem. The solution will favour satisfaction of the constraints by adding to the objective function a term that produces a high cost for violation of the limits. Therefore, the objective function can be re-defined as

\[
F = \begin{cases} 
F \text{ if } 400 \leq T_i \leq 800, & 0 \leq N_{N_i} \leq 3220 \\
-10^5 \text{ otherwise}
\end{cases}
\]  

(14)

3.3. Golden section search

The golden section search is a technique for finding the optimum point of a function by iteratively narrowing the interval containing the extremum similar to bisection brackets the zero of a function. The algorithm determining the maximum of a function \( F \) is briefly described below.

Step 1. Let \([x_l,x_u]\) be an interval containing the maximum, \( \epsilon > 0 \) be a tolerance. Set \( k = 0 \).

\[
\begin{align*}
x_l &= x_u - \phi(x_u - x_l) \\
x_u &= x_l + \phi(x_u - x_l)
\end{align*}
\]  \(\phi = (\sqrt{5} - 1)/2\)  

(15)

Step 2. Evaluate \( F(x_1) \) and \( F(x_2) \)

If \( F(x_1) \geq F(x_2) \), set \( x_u = x_2, x_l = x_1, x_l = x_u - \phi(x_u - x_l) \).

Else, set \( x_l = x_1, x_1 = x_2, x_2 = x_l + \phi(x_u - x_l) \).

Step 3. If \( x_u - x_l < \epsilon \), then the maximum occurs at \((x_l + x_u)/2\) and stop iterating, else go to Step 2.

3.4. Parameters

In this work, the parameters were obtained from the literature and summarized in Table 1.
4. RESULTS AND DISCUSSIONS

4.1. Temperature and flow rate profiles

In order to simulate and optimize the reactor, several Matlab programming files were developed based on the discussed algorithm. Figure 1 shows the profiles obtained at different top temperature ($T_0$). It is evident from the graph that the profiles are smooth and well agree with the others found in literature. It is also obtained that the proposed numerical method is stable even at the top temperature as high as 800 K, which is different from the conclusions from [8].

![Figure 1. The profiles at different top temperatures](image)

(a) $T_0=600\,\text{K}$  (b) $T_0=650\,\text{K}$  (c) $T_0=694\,\text{K}$  (d) $T_0=800\,\text{K}$
4.2. Optimization of the profit function

Figure 2 shows the variation of objective function with reactor length at different top temperatures. It can be obtained that the objective function has single maximum point at each top temperature. Therefore, the golden section search can be applied for optimization of the profit.

The optimum objective function at the top temperature of 694 K is usually found in literature [2-4, 8]. Therefore, the optimum profit at the top temperature of 694 K was also conducted and compared to the other reports. The results are showed in Table 2.

| Parameters | Babu and Angira [2] | Yusup et al. [11] | Ksasy et al. [6] | Carvalho et al. [4] | Current study |
|------------|---------------------|-------------------|-----------------|---------------------|---------------|
| x (m)      | 6.586               | 6.695             | 6.425           | 6.694               | 6.695         |
| T₀ (K)     | 406.55              | 399.85            | 308.36          | 400.00              | 400.02        |
| T_f (K)    | 5.014               | 5.017             | 5.664           | 5.016               | 5.016         |

Table 3. Optimum results

| Variables | Interval      | Optimal solution |
|-----------|---------------|------------------|
| x (m)     | [0, 10]       | 6.724            |
| T₀ (K)    | [600, 800]    | 700.27           |
| T_f (K)   | [400, 800]    | 400.00           |
| T_g (K)   |               | 629.94           |
| N₂       | [0, 3220]     | 490.68           |
| F (10⁶$/year) |         | 5.018            |

The profit return from the process depends not only the length of the reactor but also the top temperature. Therefore, the cyclic coordinate search was used for optimization the objective function. It was found that the optimum reactor length is 6.724 m and the top temperature should be operated at 700.27 K. The profit obtained from the process is $5.018 \times 10^6$ per year. The other parameters of the process are shown in Table 3. The profit value is higher than the others found in literature. The result suggests that the temperature of the feed entering the catalyst zone should be slightly higher and the reactor length is also slightly longer the other found in literature.
5. Conclusions
In this study, we presented a Runge-Kutta 4th order method for solving system of differential equation modeling the ammonia synthesis reactor. The maximum profit return was considered as multivariable optimization problem. The optimization strategy included cyclic coordinate search method for the top temperature and reactor length, golden section search for each coordinate search and barrier function for the constraints. Numerical results suggested the accuracy and efficiency of the method. The optimum solution satisfied all the constraints and higher than other reports. The synthesis system should be operated at top temperature of 700.27 K with the reactor length of 6.724 m. The corresponding economic return is $5.018 \times 10^{6}$ S/year.

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