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Optimization of an Ammonia Synthesis Reactor using Simultaneous Approach

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Ammonia is a valuable chemical produced in the industry and is wide used in the manufacture of fertilizers, plastics and pharmaceuticals. On the other hand, some important tools in chemical processes are modelling, simulation and optimization, and these types of studies have attracted considerable attention of many researchers. Several models of ammonia synthesis have been developed with the purpose of design and optimization. The typical design problem in this process requires obtained an optimal reactor length with maximum economic return and many works in literature have focused on the optimization of this reactor using different optimization techniques. In this work, an alternative approach to those presented in literature for solving this boundary value problem, and determine the optimal solution, is presented. The model of the reactor along with the kinetic form a non-linear differential-algebraic system. These differential-algebraic equations are discretized using orthogonal collocation on finite elements with continuous profiles approximated by Lagrange polynomials. In this manner, the resulting algebraic collocation equations are written as equality constraints in the optimization problem. Thus, the optimization problem is solved by implementing the IPOPT solver within the GAMS optimization-modeling platform. Although IPOPT solver here implemented is a local solver that does not guarantee the global optimum, multiple initial guesses were used to solve the problem and obtain an optimal solution of the problem. The obtained results are compared with other results available in literature and indicate that the used approach is a good alternative for dealing with this type of problems.

1. Introduction

Ammonia is a useful intermediate feedstock in the chemical industry because it is used to produce more high value-added industrial products like fertilizers, fibers, plastics, paper and pharmaceuticals. It can also be used as a refrigerant. Ammonia is commercially produced by mean the Haber-Bosch process, which is a well-established process in chemical industry. In the Haber-Bosch process, hydrogen from the steam reforming of methane is used with nitrogen taken from the air, to produce ammonia according to the reaction shows in equation 1. The exothermic reversible reaction takes place on iron promoted catalysts at high temperature and pressure in an auto-thermal manner in the ammonia converter unit, which is only a part of a complex process flowsheet, but it is considered as the heart of the whole process (Elnashaie, 1994). Several types of ammonia synthesis converters exist in the industry, e.g., TVA type ammonia converter, Horizontal multibed Kellogg reactor and Radial H. Topsøe converter (Froment et al., 2010). Many literatures discuss in detail the design and configuration of these ammonia synthesis converters. This work is particularly focused on simulation and optimization of a TVA type converter. In this way, an alternative optimization approach is presented in this work to solve a boundary value problem associated to this converter type, and find an optimal reactor length to maximize the economic return subject to a number of coupled differential-algebraic equations as constraints. This is a typical optimization problem widely studied in literature, which has been solved using different approaches like Pontryagin's maximum principle (Murase et al., 1970), Ladson's generalized reduced-gradient method (Edgar et al., 2001), genetic algorithm (Upreti and Deb, 1997), nested differential evolution (DE) (Babu

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and Angira, 2005), shooting methods (Yusup et al., 2006), gravitational search algorithm (GSA) (Borges et al., 2012) and penalty-like method (golden search) (Carvalho et al., 2014). However, all of these works employed constant properties along the reactor. In this contribution, temperature and pressure dependent properties are also included in the formulation.

$$N_2 + 3H_2 \xrightleftharpoons{catalyst} 2NH_3 \tag{1}$$

2. Mathematical Modelling

The mathematical model used in this work to describe the auto-thermal ammonia synthesis reactor is based on mass balance and energy balances for the feed and reacting gas, as follows:

- Mass balance for nitrogen

$$\frac{dN_{N_2}}{dx} = R_{N_2} = -\frac{R_{NH_3}}{2} \tag{2}$$

- Energy balance for feed gas

$$\dot{m} \cdot Cp_f \cdot \frac{dT_f}{dx} = -U \cdot A_s \cdot \left(T_g - T_f\right) \tag{3}$$

- Energy balance for reacting gas

$$\dot{m} \cdot Cp_g \cdot \frac{dT_g}{dx} = -U \cdot A_s \cdot \left(T_g - T_f\right) + \left(-\Delta H_r\right) \cdot A_t \cdot R_{N_2} \tag{4}$$

with N_{N_2} the molar flux of nitrogen, R_{N_2} the net consumption rate of nitrogen, R_{NH_3} the net production rate of ammonia, $\dot{m}$ the total mass flow rate, Cp_f and Cp_g the specific heat capacity of gas mixture in the feed and reacting gas, T_f and T_g the temperature of the feed and reacting gas, U the overall heat transfer coefficient, A_s the surface area of cooling tubes per unit length of reactor, A_t the cross sectional area of catalyst zone and ΔH_r the heat of reaction.

All of works referred above assumed the Temkin and Pyzhev rate expression based on the partial pressures of nitrogen, hydrogen and ammonia. Nonetheless, a modified form of the Temkin equation based on fugacities was presented by Dyson and Simon (1968) in order to take into account the highly non-ideal behaviour of the system due to the temperature and pressure conditions typically used in the process (around 670 K and 300 atm). In this fashion, both the Temkin equation and the modified form by Dyson and Simon (1968) were employed in this work. The modified form of the Temkin reaction rate is represented as follows:

$$R_{NH_3} = 2 \cdot k \cdot \left[K_a^2 \cdot a_{N_2} \cdot \left(\frac{a_{H_2}^3}{a_{NH_3}^2} \right)^{\alpha} - \left(\frac{a_{NH_3}^2}{a_{H_2}^3} \right)^{1-\alpha} \right] \tag{5}$$

with k the rate constant for the reverse reaction estimated by Arrhenius relation with pre-exponential factor $k_0 = 8.849 \times 10^{14}$ and activation energy $E_a = 170560 \left[kJ \cdot mol^{-1} \right]$, K_a the equilibrium constant, a_i the activity of the component i. The activity is calculated using fugacity coefficients ϕ_i and molar fractions of components y_i according to the following relation: $a_i = y_i \cdot \phi_i \cdot P$. The empirical parameter α usually takes values between 0.5 and 0.75 in literature (Dyson and Simon, 1968). In this work, $\alpha = 0.5$ was used and K_a was calculated using the Gillespie and Beattie correlation as follows (Dyson and Simon, 1968):

$$\log_{10} K_a = -2.691122 \cdot \log_{10}\left[\mathrm{T}\right] - 5.519265 \times 10^{-5} \cdot \mathrm{T} + 1.848863 \times 10^{-5} \cdot \mathrm{T}^2 + 2001.6 \cdot \mathrm{T}^{-1} + 2.6899 \tag{6}$$

The fugacity coefficients of nitrogen, hydrogen and ammonia can be determined by semi-empirical equations that are temperature and pressure dependent according to Dyson and Simon (1968). These expressions are extremely nonlinear and may cause difficulty in the computation. In addition, the rate expression must also be multiplied by an effectiveness factor η to take in into consideration the intraparticle mass transfer resistance

through the interior of the catalyst pellet. This effectiveness factor was calculated from the following empirical correlation (Dyson and Simon, 1968):

$$\eta = b_0 + b_1 \cdot T + b_2 \cdot X_{N_2} + b_3 \cdot T^2 + b_4 \cdot X_{N_2}^2 + b_5 \cdot T^3 + b_6 \cdot X_{N_2}^2 \tag{7}$$

with X_{N_2} the conversion based on nitrogen. Constants b_i in this relation were given by Dyson and Simon (1968) at different pressures. It is worth mentioning that all of optimization results obtained in those works mentioned in introduction have been based on a pseudo-homogeneous model with intrinsic rate of reaction. Therefore, the optimal policy obtained is not truly optimal because the effectiveness factor for ammonia synthesis is between 0.3-0.5 (Elnashaie and Alhabdan, 1989), and this factor was not included in formulation in these works. Finally, the polynomial equations reported by Shah (1967) to express the temperature and pressure dependence of the heat capacities for all involved species were used in this work. In addition, the enthalpy of reaction also depends on the pressure and temperature; in this case, it was calculated using the heat capacities.

3. Optimization Methodology

The objective function of the optimization problem considered in this work is the economic return 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. This is the same objective function as in those works previously mentioned. This objective function was first derived by Murase et al. (1970); however, a correction to Murase's formulation can be found in Upreti and Deb (1997). The final expression is as follows:

$$f\left(x, N_{N_2}, T_f, T_g\right) = 1.33563\times10^7 - 1.70843\times10^4 \cdot N_{N_2} + 704.09 \cdot \left(T_g - T_0\right) - 699.27 \cdot \left(T_f - T_0\right) - \sqrt{3.45663\times10^7 + 1.98365\times10^9 \cdot \mathrm{x}} \tag{8}$$

The equality constraints of this optimization problem are the differential-algebraic equations (DAEs) distributed in space presented in the previous section, which leads to a DAE-constrained optimization problem. These DAEs are highly non-linear because of the reaction rate equation based on the activity of components. An effective way of dealing with this kind of optimization problem is carrying out a full discretization of the DAE system and incorporating the discretized DAEs into an NLP formulation. A robust method of discretization was employed in this work to deal with the high nonlinearity of the system caused by the reaction rate used. In this fashion, the orthogonal collocation on finite elements (OCFE) method was used in this work, along with Radau collocation points because of their compatibility with the NLP formulations and desirable stability properties (Biegler, 2010). Finally, the applied methodology leads to a set of nonlinear algebraic equations (NLP problems), and these usually require efficient solution strategies. Thus, a robust and efficient NLP solver must be chosen for solving the optimization problem. In consequence, IPOPT solver, which is a solver based on interior-point methods was implemented, and the problem was formulated within GAMS optimization modelling platform. More details on the background of this methodology can be found in Biegler (2010).
Inequality constraints were also included in the optimization based upon the upper and lower bounds of the design and operation variables, in accordance with industry, as follows:

$$0 < x \le 10\ ; \quad 400 \le T_f \le 800\ ; \quad 0 \le N_{N_2} \le 3220 \tag{9}$$

Finally, just like most of works in literature that have focused on this optimization problem, the only decision variable considered in this study was the reactor length. However, other decision variables like inlet feed temperature, top temperature, feed rate of gas, ammonia and inert content of the feed gas or hydrogen to nitrogen ratio in the feed can also be considered in the optimization.

4. Results and Discussion

Initially, only a simulation of the reactor was considered in order to provide an appropriate number of finite elements and collocation points in the used discretization method, and demonstrate the effectiveness of the proposed strategy.

Table 1: Specifications of the simulated reactor

Parameter	Units	Value
Reactor length	m	5.18
Reactor pressure	atm	286
Top temperature	K	694.15
Inlet mass flow rate	$kg \cdot h^{-1}$	26,400
Cross sectional area of catalyst zone	m^2	0.78
Surface area of cooling tubes per unit length of reactor	m	10
Overall heat transfer coefficient	$J \cdot m^{-2} \cdot s^{-1} \cdot K^{-1}$	581.8
Specific heat capacity of feed gas	$kJ \cdot kg^{-1} \cdot K^{-1}$	2.96
Specific heat capacity of reacting gas	$kJ \cdot kg^{-1} \cdot K^{-1}$	3.01
Heat of reaction	$kJ \cdot mol^{-1}$	-112.97
Catalyst activity	−	1.0

Feed Compositions, Mole Fraction

H_2	N_2	NH_3	CH_4	Ar
0.6525	0.2175	0.05	0.04	0.04

Table 1 summarizes the specifications of the industrial ammonia synthesis converter used here, which were taken from Murase et al. (1970). Such simulation was implemented in GAMS considering a dummy objective function and without decision variables; therefore, a square system of non-linear collocation and continuity equations were solved without any degrees of freedom. As can be noted from Table 1 the thermodynamic properties are constant; however, simulations with constant properties and temperature and pressure dependent properties were carried out in this work. A comparison between both simulations can be seen in Figure 1. In the case of constant properties the exit ammonia mole concentration was 0.2011, which is in good agreement to the value reported by Murase et al. (1970), which was 0.2007. Additionally, the temperature profiles of the feed and reacting gas were also very similar to those presented in Murase et al. (1970). It is important to highlight that a great advantage of having carried out these simulations in GAMS, it is that the obtained results can be used as consistent initial guesses for states in the optimization problem. In these simulations, 2, 5, 10 and 15 finite elements with 3 Radau collocation points were tested in order to verify the consistency of the results. The obtained profiles were the same qualitatively with small quantitative differences for the simulation with 2 finite elements. These results prove the robustness of the OCFE regardless the number of elements for this specific problem. In this way, it is recommended to use at least 5 finite elements in order to get smoother profiles. Using IPOPT, the solutions took 0.7, 0.8, 1.0 and 1.2 CPUs (4GB and 2.2GHz HP laptop) for 2, 5, 10 and 15 elements for the simulation with constant properties; and 0.8, 1.3, 1.6 and 2.3 CPUs for the simulation with dependent properties, respectively.

After simulation were performed, these solutions were used as initial guesses of states and given to the optimization problem. As before, a solution obtained with constant properties has been plotted in Figure 2 with the collocation solution of dependent properties at the optimal parameter values.

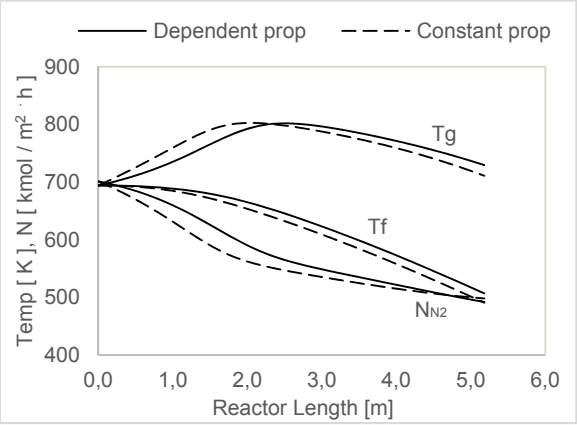

Figure 1: Simulated profiles with constant and dependent properties

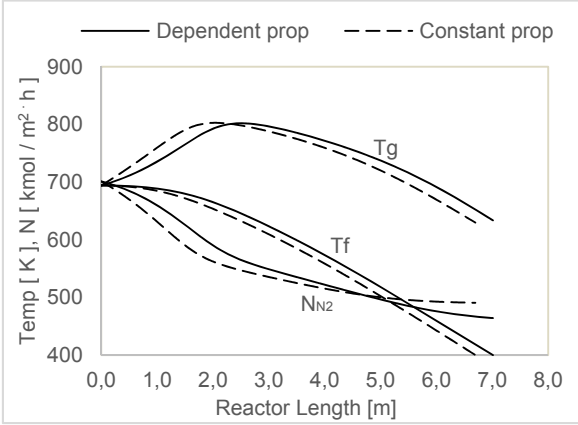

Figure 2: Optimal profiles with constant and dependent properties

Table 2: Comparison between optimal results with constant and dependent properties

Optimized parameter	Constant Properties ; Temkin reaction rate	Dependent. Properties; Dyson and Simon reaction rate
Reactor length [m]	6.695	7.012
Molar flux of nitrogen [kmol / $m^2 \cdot h$]	490.75	464.24
Feed gas temperature [K]	400.00	400.00
Reacting gas temperature [K]	629.72	633.57
Objective Function [$ / y]	$5.0175 \cdot 10^6$	$5.4705 \cdot 10^6$

After applying the full discretization approach to the DAE model with 3 Radau collocation points and 10 finite elements, NLP problems were obtained as follows: NPL with constant properties (349 variables and 348 equality constraints); NPL with dependent properties (1368 variables and 1367 equality constraints), both with 1 degrees of freedom. Using GAMS, the optimal solutions were obtained in 1.4 and 3.1 CPUs (4GB and 2.2 GHz HP laptop) with 14 and 29 iterations of IPOPT solver respectively. Again, differences in the profiles are observed in Figure 2. These differences can be better appreciated quantitatively in Table 2, where can be observed an increase of 9 % in the profit (objective function) and a corresponding increase of 5 % in the optimal reactor length for the case of dependent properties and when used the modified Temkin rate equation. In the optimizations, two different approaches were employed to determine the initial guesses. The first one is a method starting from scratch, in which no initial values or initial values beyond the lower and upper boundaries were employed for states; the second one was to take as initial values the results from simulations. The final optimal results were the same using both approaches for initialization; however, with the second initialization method the response was obtained with a smaller number of iterations and in less CPU time.

Table 3 shows a comparison between optimal results obtained in this work assuming constant properties and results reported in previous studies available in literature at the same conditions as used here. The values of objective function and reactor length show similarities with the most of recent studies. With the older ones (Murase et al., 1970; Upreti and Deb, 1997; Edgar et al., 2001), however, there is a huge difference with the optimal values computed in this work. These differences is explained because these works had some errors in formulation, which were corrected in subsequent works (Babu and Angira, 2005). Therefore, the optimal values reported in these works are wrong. In this fashion, the approach considered in this work is able to estimate satisfactorily both the maximum economic return and the optimal reactor length when compared with other results reported in literature.

5. Conclusions

In this work, an alternative approach for solving a typical problem of optimal design in an ammonia converter to give maximum economic return is presented. Thus, from the successful optimization of this problem can be concluded that the methodology developed and applied in this work is able to provide reliable results when compared with previous results reported in literature, verifying the accuracy and efficiency of the full discretization approach for DAE-constraint optimization problems.

Table 3: Comparison of optimal results with previous studies

Approaches	Reactor length [m]	Objective Function [$ / y]	Feed gas temperature [K]	Reacting gas temperature [K]	Molar flux of nitrogen [kmol / $m^2 \cdot h$]
Murase et al. (1970)	4.290	Not reported	Not reported	747.15	522.15
Edgar et al. (2001)	2.580	$1.2880 \cdot 10^6$	478	563	625
Upreti and Deb (1997)	5.320	$4.2300 \cdot 10^6$	Not reported	Not reported	Not reported
Babu and Angira (2005)	6.586	$5.0068 \cdot 10^6$	Not reported	Not reported	Not reported
Yusup et al. (2006)	6.695	$5.0150 \cdot 10^6$	400.00	629.65	490.84
Borges et al. (2012)	6.695	$5.0150 \cdot 10^6$	400.00	629.65	490.84
Carvalho et al. (2014)	6.694	$5.0158 \cdot 10^6$	400.00	629.71	490.79
This work	6.695	$5.0175 \cdot 10^6$	400.00	629.72	490.75

On the other hand, the OCFE method implemented has shown to be computationally efficient in terms of CPU time. Therefore, this optimization approach has great potential for real applications and can be successfully applied to theoretical studies on highly non-linear and complex engineering problems.

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