Modeling and Optimization of Ammonia Reactor using Shooting Methods

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Abstract:- Ammonia production depends on temperature of feed gas at the top of the reactor (top temperature), the partial pressures of the reactants and the reactor length. The optimal design problem requires obtaining the optimal reactor length with maximum economic returns corresponding to a top temperature of 694K. This paper presents an alternative approach in solving the boundary value problem and at the same time determines the optimal solution. Shooting methods, namely single and multiple-shooting methods are used. The software used for this modeling is MATLAB version 6.1. The ordinary differential equation (ODE) integration routine technique used is 'ode45' and the optimization routine of 'FMINCON' is selected for multiple-shooting. The profiles of N_{N_2}, T_f *and* T_g *at a top temperature of 694K were generated. From the results obtained, this temperature yields an objective function value of \$5.015 x* 10^6 *per year at an optimum reactor length of 6.695m. The objective function and reactor length values agree with the latest literature work using Differential Evolution (DE) approach, and multiple-shooting performs better than single-shooting under bad initial guesses of the reactor length.*

Keywords: *Single-shooting, Multiple-shooting, Ammonia Reactor Optimization, Reactor Length*

1 Introduction

Ammonia is a major commodity chemical. Most of the world's ammonia production is used for fertilizers. It is also used in the manufacturing of explosives and other important chemicals and products. As a result of that, modeling and optimizing ammonia synthesis has received a lot of attention among the process industries. In modern ammonia plants, ammonia is produced based on Haber's process:

$$3\ H_2\ (g) + N_2\ (g) \longleftrightarrow 2\ NH_3\ (g)$$
$$\Delta H = -92\ KJ/mol$$

Ammonia synthesis using the Haber process is restricted by unfavourable position of the chemical equilibrium and by the relatively low activity of the promoted iron catalysts. Even at high pressures such as 30 MPa, not more than 20-25% of the synthesis gas is converted to ammonia per pass. The unreacted gas mixture is returned to the reactor. The production of ammonia depends on the temperature of the feed gas at the top of the reactor i.e. top temperature, the partial pressures of the reactants, and the reactor length. The optimal design problem requires obtaining the optimal reactor length with maximum economic returns corresponding to the various top temperatures. Simulation models for ammonia synthesis converters of different types have been developed for design & optimization [1, 2, 3, 4].

According to Babu, B.V et. al [4], Upreti, et. al [3] used Murase's formulation with correct objective function and correct stoichiometric expressions of the partial pressures of N_2, H_2 and NH_3. Upreti, et. Al [3] used simple GA in combination with GEAR package of NAG library's subroutine, D02EBF, for the optimization of ammonia synthesis reactor. However, there is a contradiction in the

temperature and gas flow rate profiles obtained. Babu, B.V et. al [4] claimed that DE is an improved version of simple GA which is faster, robust and more likely to a function's true global optimum. They used Nested DE in choosing the right combination of the DE key parameters. This paper presents an alternative approach using shooting methods to determine the optimal reactor length and system's objective function subject to a number of equality constraints involving solution of coupled differential equations.

2. Problem Formulation

The formulation used in this paper is similar to Babu, B.V et. al [4] and Upreti, et. al [3]. In the study by Upreti, et. al [3] by using GAs, it is found that for the range of top temperature of the reactor (from 668K to 706K), the profit corresponding to the optimal reactor length is increased monotonically. The optimal reactor length at a top temperature of 668K increases from 0.63m to5.31m. Typical economic return from the reactor operation with a top temperature of 694K an d 5.33m reactor length is about \$4.23 x 10^6 per year. Babu et. al [4] extended the study on the optimization of an auto-thermal ammonia synthesis reactor design by using DE method. They solved three-coupled differential equations using NAG subroutine (D02EJF) in MATLAB. The step sizes of 0.01 and 0.001 are used instead of that used by Upreti et. al. [3] who used only 0.01.The optimization Quasi-Newton (QN) method is used along with the above subroutine. The results of their study give an optimum reactor length of 6.79m with a top temperature of 694K and an optimum objective function of \$4.84 x 10^6 per year.

The current work proposes an alternative way to determine the optimal value of objective function and reactor length using the shooting methods (single and multiple shootings). The following assumptions were made to simplify the development of the ammonia reactor model:

- The rate expression is valid
- Longitudinal heat and mass transfer can be ignored
- The gas temperature in the catalytic zone is also the catalyst particle temperature
- The heat capacities of the reacting gas and feed gas remains constant
- The catalytic activity is uniform along the reactor and equal to unity
- The pressure drop across the reactor is negligible compared with the total pressure in the system

2.1 Objective Function

The objective function depicts the economic return based on the difference between the value of the product gas and the feed gas less the amortization of reactor capital costs. Similar objective function for the process is adopted from Babu, B.V et. al [4];

$$f(x, N_{N_2}, T_f, T_g) = 1.33563\times10^7 - 1.70843\times10^4 N_{N_2} + 704.09(T_g - T_0) - 699.27(T_f - T_0) - [3.45663\,\mathrm{x}\,10^7 + 1.98365\,\mathrm{x}\,10^9 x]^{1/2} \quad (1)$$

2.2 Energy Balance Equation

Equations (2)-(6) are the energy balances that need to be satisfied in order to get the value of the three variables: T_f, T_g and N_{N_2}.

$$\frac{dT_f}{dx} = \frac{US_1}{WC_{pf}}(T_g - T_f) \quad (2)$$

$$\frac{dT_g}{dx} = \frac{US_1}{WC_{pf}}(T_g - T_f) + \frac{(-\Delta H)S_2}{WC_{pg}}\left(\frac{-dN_{N_2}}{dx}\right) \quad (3)$$

$$\frac{dN_{N_2}}{dx} = -f\left(k_1\frac{p_{N_2}p_{H_2}^{1.5}}{p_{NH_3}} - k_2\frac{p_{NH_3}}{p_{H_2}^{1.5}}\right) \quad (4)$$

where

$$k_1 = 1.78954\times10^4 \exp\left(\frac{-20800}{RT_g}\right) \quad (5)$$

$$k_2 = 2.5714\times10^{16} \exp\left(\frac{-47400}{RT_g}\right) \quad (6)$$

2.3 Equality Constraints

The partial pressures that appear in the above energy equations are computed as shown in equation (7):

$$p_{N_2} = \frac{286 N_{N_2}}{2.598 N_{N_2} + 2 N_{N_2}}$$

$$p_{H_2} = 3 p_{N_2}$$

$$p_{NH_3} = \frac{286(2.23 N_{N_{20}} - 2 N_{N_2})}{2.598 N_{N_{20}} + 2 N_{N_2}}$$

The boundary conditions are:

$$T_f(x=0) = T_0; \qquad T_g(x=0) = T_f;$$

$$N_{N_2}(x=0) = 701.2 \frac{kmol}{m^2 h}$$

2.4 Inequality Constraints

The upper and lower bounds of the design variables are as follows:

$$0 \frac{kmol}{m^2 h} \le N_{N_2} \le 3220 \frac{kmol}{m^2 h} \ ;$$

$$400K \le T_f \le 800K \ ; \ 0m \le x \le 10m$$

Since the reaction gas temperature (T_g) depends on the nitrogen mass flow rate (N_{N_2}), feed gas temperature (T_f) and reactor length (x), there is no need to implicate any boundaries on T_g. Fig 1-3 show illustrations of multiple shooting method with 2, 4 and 8 intervals respectively. Table 1,2, and 3 list the initial conditions and guesses for all variables used in the modeling for multiple shooting with 2, 4 and 8 intervals respectively.

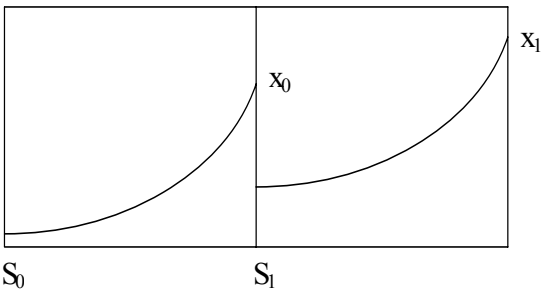

Fig. 1: Illustration of multiple shooting with 2 intervals

Table 1: Initial Condition (S0, S1) and Initial Guessed (X0 and X1) Values for multiple shooting with 2 intervals

	S_0	**X_0**	**S_1**	**X_1**
N_{N_2} **(kmol/m²h)**	701.2	500	510	450
T_f (K)	694	540	550	410
T_g (K)	694	725	730	430

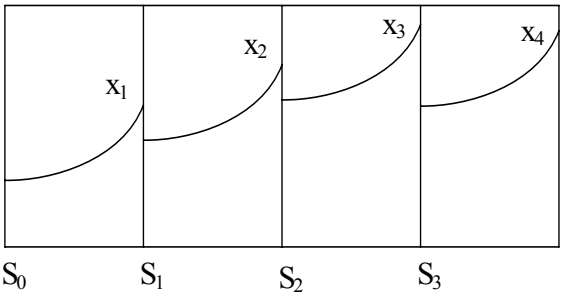

Fig. 2: Illustration of multiple shooting with 4 intervals

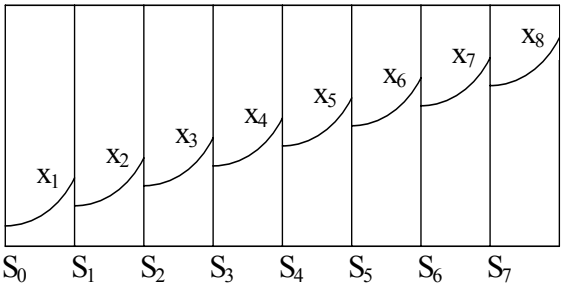

Fig. 3: Illustration of multiple shooting with 8 intervals

Table 2: Initial Condition (S0, S1) and Initial Guessed (X0 and X1) Values for multiple shooting with 4 intervals

	S_0	X_1	S_1	X_2	S_2	X_3	S_3	X_4
N_{N_2} **(kmol/m^{2}h)**	701.2	550	540	505	500	498	498	490
T_f (K)	694	640	635	505	500	370	360	200
T_g (K)	694	800	790	730	725	600	590	420

Table 3: Initial Condition (S0, S1) and Initial Guessed (X0 and X1) Values for multiple shooting with 8 intervals

	S_0	X_1	S_1	X_2	S_2	X_3	S_3	X_4	S_4	X_5	S_5	X_6	S_6	X_7	S_7	X_8
N_{N_2} **(kmol /m^{2}h)**	701.2	610	600	550	545	510	505	503	500	498	496	495	494	493	492	491
T_f (K)	694	675	670	635	630	575	570	505	500	415	410	370	365	280	275	200
T_g (K)	694	765	770	800	790	760	755	730	725	660	650	600	590	500	490	420

3. Methodology

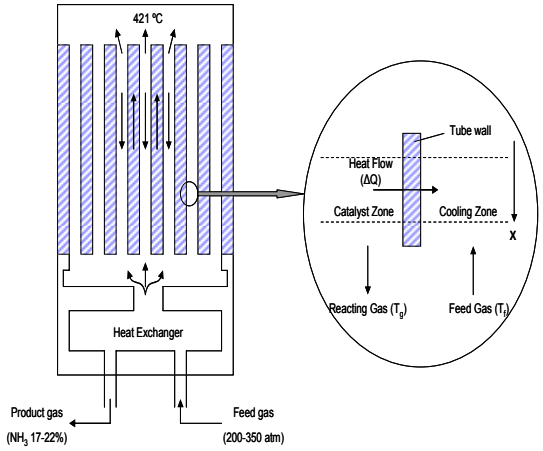

Fig. 4 : Schematic diagram of an ammonia react

Figure 4 shows the schematic diagram of the ammonia reactor studied. The feed gas with nitrogen (21.75 mole %), hydrogen (62.25 mole %), ammonia (5 mole %), methane (4 mole %), and argon (4 mole %) enters the bottom of the reactor and is preheated by the counter-current flowing reaction gas before reversing its flow to undergo reversible exothermic reaction in the catalyst basket where ammonia is produced. The reacted gas that consists of unconverted nitrogen and hydrogen, ammonia and inert will react with the entering feed gas before leaving at the bottom of the reactor. The objective function depends on four variables (x, N_{N_2}, T_f and T_g).

There are three differential equations and four variables, making the degree of freedom equal to one. By specifying the length of reactor, the remaining variable can be calculated using the system model and set these variables as an input to the optimization routine as shown in Figure 5.

The software used for modeling is MATLAB Version 6.1 and the methods used to solve the objective function are multiple shooting method.

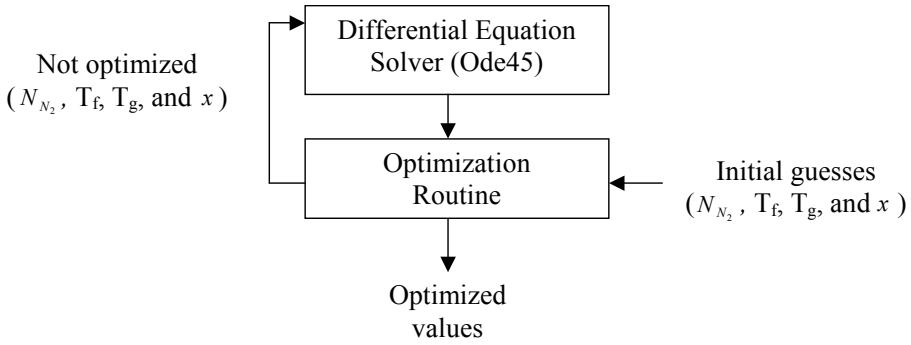

Fig.5 : Computational procedures

3.1 Single-Shooting Method

Single shooting method is a simple method to solve a two-point boundary-value problem. A general two point boundary-value problem can be written as shown below;

$$\frac{dy}{dx} = f(x, y); a \le x \le b$$

$$Ay(a) = \alpha \ , \ By(b) = \beta$$

where A and B are $m \times n$ matrices with rank (A) + rank (B) = n

A study for solving two-point boundary-value problem was done by R. Holsapple, R. Venkataraman and D. Doman, (2003). By converting equation (5) into an initial-value problem (IVP);

$$y(a) = y_a$$

where y_a is composed of known states from $Ay(a) = \alpha$ and guesses for the unknown s_0.

Now, $y(x) \in \Re^n$, $\alpha \in \Re^m$, $\beta \in \Re^p$. Let $s_0 \in \Re^{n-m}$ be the guess for the unknown initial conditions and s_k, where k ≥ 1 subsequent corrections of the vector s_0. Integration can then be performed from point $x = a$ to $x = b$. The error, $e = \left\| By(b) - \beta \right\|^2$ is then computed to make correction to the initial guess s_0 to yield s_1. This integration is repeated over again until $e < \varepsilon$, where $\varepsilon > 0$ is small.

Single shooting method represents a pure sequential approach whereas multiple shooting is considered as a hybrid approach because the model equations are solved "exactly" only on intervals during the solution iterations. Therefore direct single shooting method only requires two boundary initial value guesses (i.e. a and b) whereas multiple shooting approach requires initial guesses for all the node values (i.e. x_1, x_2 and x_3). The disadvantage of single shooting method is there can be serious problems with the accuracy. The problems occur when making the correction to the calculated vector. This vector is usually corrected using a modified Newton's Method and in practice, the system must be linearized to use this method. If error is large, then convergence can be quite slow. This drawback can be fixed by implementing multiple-shooting method.

3.2 Multiple Shooting Method

Multiple-shooting serves as a bridge between sequential approaches and simultaneous approaches. This technique has the same underlying approach as single shooting, but the integration is done over many intervals where in this case refers to the length of the ammonia reactor. The TWO main steps in carrying out this technique are;

i) control representation/ discretization
ii) state discretization by multiple-shooting

For multiple-shooting (Fig. 1-3), the length of the reactor is partitioned into smaller length elements and the differential algebraic equation (DAE) models are integrated separately in each element.

Equality constraints are added to the nonlinear program in order to link the elements and ensure that the states are continuous across each element. Inequality constraints for states and controls can be imposed directly at the grid points.

In multiple-shootir _ strategy, the following general dynamic optimization problem is considered:

$$Min \qquad \varphi(z(t_f), x(t_f), u(t_f), t_f, \theta) \quad (1)$$

$$z(t), x(t), u(t), t_f, \theta$$

Subject to DAE model:

$$\frac{dx}{dt} = f(z(t_f), x(t_f), u(t_f), t_f, \theta) \quad , \ t \in I \qquad (2)$$

where $0 = G(z(t), x(t), u(t), t, \theta)$, $t \in I$

Initial conditions:

$$x(0) = x_0 \qquad (3)$$

As well as general inequality constraints (state and control):

$$0 \le h(z(t), x(t), u(t), \theta) \qquad (4)$$

In addition, terminal constraints (if any):

$$0 = r(x(t_f)) \qquad (5)$$

The functions *f, G, h* and *r* are assumed to be twice continuously differentiable, $t_f > t_0$, and the initial conditions x_0 and the model parameters are known and fixed. The following paragraph shows the steps involved in the application of multiple shooting method.

Step 1: Control representation/ discretization

Let the initial time horizon $I = \lfloor t_0, t_f \rfloor$

Divide into N subintervals,

$$I_i = [\tau_i, \tau_{i+1}] \qquad (6)$$

for $i = 0,1,\ldots,N-1$

and $t_0 < \tau_1 < \ldots < \tau_N < t_f$

Hence the control trajectory is then parameterized bv a piecewise approximation of t ł control u_i defined by

$$u_i = \gamma_i(\tau, q_i) \quad \text{for } \tau \in [\tau_i, \tau_{i+1}] \qquad (7)$$

using N local control parameter vectors q_i, where $q_0, q_1, \ldots, q_{N-1}$

The functions γ_i are given basic functions, typically vectors of polynomials. If piecewise constant approximation is chosen, then $\gamma_i(\tau, q_i) = q_i$.

Step 2: State discretization by multiple shooting

Introduced N+1 additional vectors $s_0, s_1, .., s_N$, where s_i = combination of s_i^z and s_i^x. The dimension is the same as the system state. These are also known as "multiple shooting node values". All but the last value serve as initial values for the resulting N independent decoupled IVP on the intervals I_i:

$$\frac{dx_i}{d\tau} = f_i(z_i(\tau), x_i(\tau), \gamma_i(\tau, q_i), \theta)$$

$$\text{for } \tau \in [\tau_i, \tau_{i+1}] \qquad (8)$$

$$0 = G_i(z_i(\tau), x_i(\tau), \gamma_i(\tau, q_i), \theta) \qquad (9)$$
$$- G_i(s_i^x, s_i^z, \gamma_i(\tau, q_i), \theta$$

$$x_i(\tau_i) = s_i^x \qquad (10)$$

$$z_i(\tau_i) = s_i^z \qquad (11)$$

Additional constraints:

1- The decoupled IVP are connected by continuity (or matching) conditions, i.e. each node value should equal the final

value of the preceding trajectory:

$s^x_{i+1} = x_i(\tau_{i+1}; s_i, q_i)$,

$i = 0, 1, ... N-1$

2- The first multiple shooting node variable s_0 must be equal to the initial value x_0 of the optimization problem (this applies only when we are considering optimal trajectory problems, otherwise this is not a necessity), $s^x_0 = x_0$.

The constraints are not necessarily satisfied during the optimization iterations. Multiple shooting can deal with infeasible initial guesses of the variables s_i and q_i.

The algebraic equations (i.e. equation (9)) in each multiple shooting interval have an additional subtrahend term. This is called as a relaxed version of the original DAE and allows for inconsistent initial values s^x_i and s^z_i.

Summarizing, the finite dimensional NLP in the direct multiple shooting parameterization is given by:

$$Min \quad \sum_{i=0}^{N-1} L_i(s^i{}_x, s^i{}_z, \gamma_i(\tau, q_i), \theta) + E(s^x{}_N, \theta) \qquad (12)$$

q, s

The expression in (12) is further minimized subject to the following continuity conditions:

$$s^x{}_{i+1} = x_i(\tau_{i+1}), \text{ for } i = 0,1,\ldots,N-1 \qquad (13)$$

initial conditions:

$$s^x{}_0 = x_0 \qquad (14)$$

consistency conditions:

$$0 = G(s_i{}^x, s_i{}^z, \gamma_i(\tau, q_i), \theta, \text{ for } i = 0,1,\ldots,N \qquad (15)$$

Control and path constraints are imposed point-wise at the multiple shooting nodes:

$$h(s_i{}^x, s_i{}^z, \gamma_i(\tau, q_i), \theta) \geq 0, \text{ for } i = 0,1,\ldots,N \qquad (16)$$

as well as terminal point (if any)

$$0 = r(s_N) \qquad (17)$$

To carry out both shooting strategies, MATLAB version 6.1 is chosen as the platform for the implementation, utilizing the ODE integration routine plus the optimization solver available.

4. Results and Discussions

4.1 Single Shooting

Four MATLAB programming files were developed to model and optimize the ammonia reactor. From the profiles obtained, it is found out that the optimum reactor length is 6.695m and the corresponding objective function is \$5.015 x 10^6 per year. The corresponding values of N_{N_2}, T_f and T_g are shown in Table-4.

4.2 Multiple-Shooting

For multiple shooting, four MATLAB programming files were developed to model and optimize the ammonia reactor. Figures 8, 9 and 10 shows the resulting profiles at different number of intervals. Data from the graphs are shown in Tables 5, 6 and 7 respectively.

From Table-8, it is clear that irrespective of the number of interval, the same optimized values for objective function (\$5.015 x 10^6 per year) and reactor length (6.695m) were obtained. This consistency authenticates the robustness of the multiple shooting method regardless the number of intervals.

Various initial guesses of N_{N_2}, T_f, T_g and reactor length, x have been used to test the robustness for this multiple shooting method including initial guesses which are beyond the upper and lower boundaries. It is found that for multiple shooting, regardless the initial guess values of reactor length, the objective function and optimum reactor length remain the same. Hence, this shows that multiple shooting is robust in solving non-linear programming problems.

Table-4: Results obtained from optimization using single-shooting

Reactor Length, z (m)	N_{N_2} **(kgmol/m^{2}h)**	**T_f (K)**	**T_g (K)**
0	701.20	694	694
6.695	490.84	400	629.65

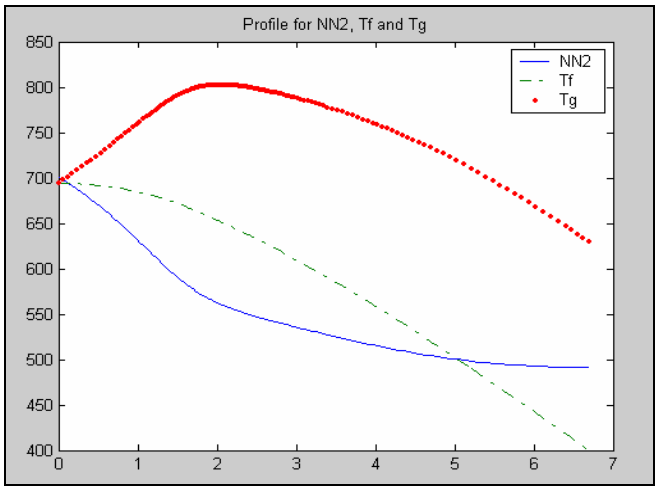

Fig. 7: Profiles for single shooting

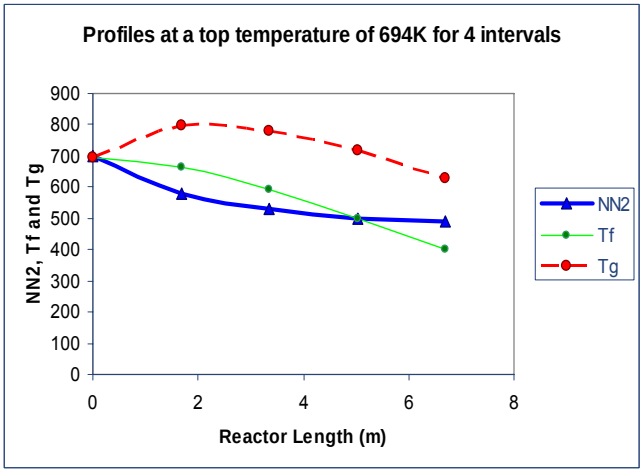

Fig.9 : Profiles for four intervals using multiple shooting

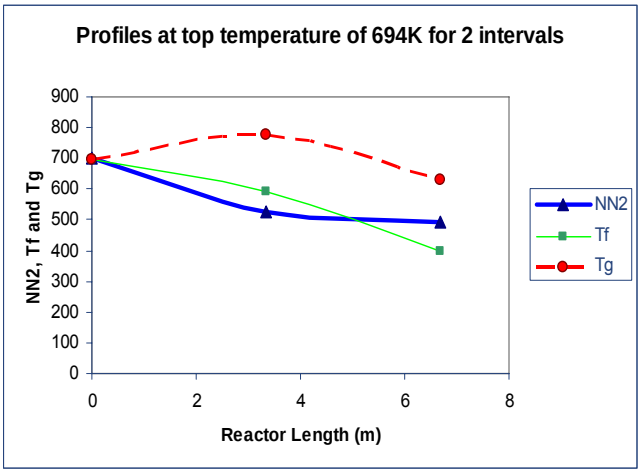

Fig.8 : Profiles for two intervals using multiple-shooting

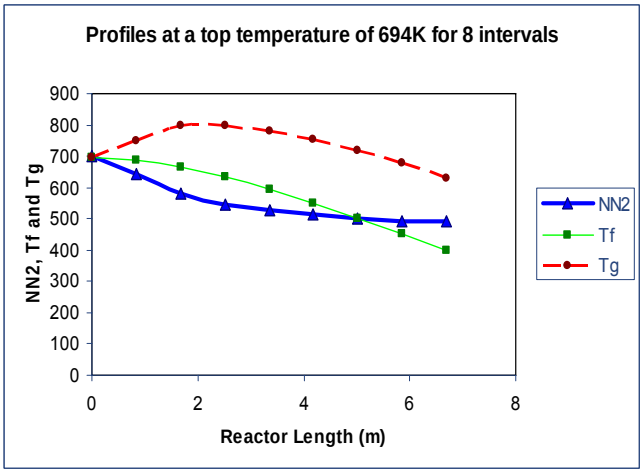

Fig.10: Profiles for eight intervals using multiple-shooting

Table-5: Results obtained from optimization for two intervals

Reactor Length, z (m)	N_{N_2} **(kgmol/m^{2}h)**	T_f **(K)**	T_g **(K)**
0	701.20	694	694
3.348	528.14	592.39	778.97
6.695	490.84	400	629.65

Table-6: Results obtained from optimization for four intervals

Reactor Length, z (m)	N_{N_2} **(kgmol/m^{2}h)**	T_f **(K)**	T_g **(K)**
0	701.20	694	694
1.674	578.79	665.89	797.14
3.348	528.14	592.39	778.97
5.021	500.09	501.20	719.10
6.695	490.84	400	629.65

Table-7: Results obtained from optimization for eight intervals

Reactor Length, z (m)	N_{N_2} **(kgmol/m^{2}h)**	T_f **(K)**	T_g **(K)**
0	701.20	694	694
0.837	644.81	687.65	748
1.674	578.79	665.89	797.14
2.511	546.83	631.97	797.93
3.348	528.14	592.39	778.97
4.185	512.08	548.49	752.98
5.021	500.09	501.02	719.10
5.858	493.45	451.14	677.15
6.695	490.84	400	629.65

Table-8: Summary of number of intervals, time taken, profit and optimal reactor length for initial guess of 7m.

Number of intervals	**Number of iterations**	**Time taken for optimizer to terminate successfully (s)**	**Objective function, ($/yr)**	**Optimal Reactor Length (m)**
2	4	2.17	5.015 x 10^6	6.695
4	5	5.83	5.015 x 10^6	6.695
8	5	19.00	5.015 x 10^6	6.695

4.3 Comparison With Previous Studies

A top temperature of 694K is the top temperature of interest in previous optimization studies [4]. Hence, this temperature is the benchmark for initial condition for the shooting methods. By comparing the result with previous studies, the objective function and reactor length values show similarities with the study done by Babu, B.V et. al [4] using Gear's method (GEAR) with Differential Evolution (DE) – see Table 9. The result given by shooting strategies as found in this study agrees considerably well with the values as reported by [4].

Table 9: Optimum reactor length and objective function values comparison

Methods used	**Optimal Reactor Length, (m)**	**Objective function value, ($/yr)**
GEAR with DE [4]	6.790	4.848×10^6
Single Shooting	6.695	5.015×10^6
Multiple Shooting	6.695	5.015×10^6

4.4 Single Shooting Vs. Multiple Shooting

Varies initial guesses of N_{N_2}, T_f, T_g and reactor length, x have been used to test the robustness for both method including initial guesses which are beyond the upper and lower boundaries. It is found that single shooting fails when reach to a reactor length of 17m. For multiple shooting, this failure does not exist. Hence, this shows that multiple shooting is more stable than single shooting in solving non-linear programming problems.

Table-10: Comparison in robustness and stability of both shooting methods

Initial guess of reactor length (m)	**Single Shooting**		**Multiple Shooting**	
	Objective Function	Reactor Length (m)	Objective Function	Reactor Length (m)
10	$\$5.015 \times 10^6$ / year	6.695	$\$5.015 \times 10^6$ / year	6.695
15	$\$5.015 \times 10^6$ / year	6.695	$\$5.015 \times 10^6$ / year	6.695
17	Failed	Failed	$\$5.015 \times 10^6$ / year	6.695

5. Conclusion

In this study, an alternative approach of solving an optimal design problem for an ammonia reactor to give maximum economic using shooting methods has been carried out. Both shooting methods have been demonstrated to be able to give accurate results of reactor length 6.695m with corresponding profit of $\$5.015 \times 10^6$ per year. These values agree considerably well with those obtained by recent study of Babu, B.V et. al [4] using different approach. It has also been found that by increasing number of intervals, the robustness of multiple-shooting strategy increases in comparison with single-shooting, especially to poor initial guesses. The convergence time also increases with respect to the number of intervals. This successful application of the multiple-shooting method for the optimal design of ammonia synthesis reactor indicates that this approach has great potential and can be applied to advantage in all the highly non-linear and complex engineering problems.

6. Nomenclature

Variables	
x (independent)	Reactor Length, m
N_{N2}	Mole flow rate of N2 per area catalyst, kg mol/(m2 h)
T_f	Temperature of feed gas, K
T_g	Temperature of reacting gas,K

Parameters	
C_{pf}	Heat Capacity of the feed gas = 0.707 kcal/kgK
C_{pg}	Heat Capacity of reacting gas = 0.719 kcal/kgK
$f()$	Objective function $/year
f	Catalyst activity = 1.0
ΔH	Heat of reaction = -26 000 kcal/kg mol N2
N	Mass flow of component through catalyst zone, kg mol/m2.h
N_1	Hours of operation per year, 8330
p	Partial pressure of component, psi and reactor pressure is 286 psia
R	Ideal gas constant, 1.987 kcal/kg mol K
S_1	Surface area of catalyst tubes per unit length of reactor = 10m
S_2	Cross sectional area of catalyst zone = 0.78 m2
T_o	Reference temperature = 421˚C(694 K)
U	Overall heat transfer coefficient = 500 kcal/hm2K

W	Total mass transfer flow rate = 26 400 kg/ h
φ	A scalar objective function
f	Differential equation constraints
G	Algebraic equation constraints
x	Differential state profile vectors
z	Algebraic state profile vectors
u	Control state profile vectors
θ	A time-dependent parameter vector
r	Describes the end-point constraints
I	The fixed time horizon being considered

7. References

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