Optimal Design of Ammonia Synthesis Reactor

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Abstract

In this work, an optimization framework is used to obtain useful model for an ammonia synthesis reactor that can be confidently applied to reactor design, operation and control. The main objective in the optimal design of such reactor is the estimation of the optimal reactor length for obtaining the maximum profit from the reactor at the best top temperature with satisfying the process constraints. gPROMS package has been used for modelling, simulation and optimal design via optimization.

The optimization problem is posed as a Non-Linear Programming (NLP) problem and is solved using a Successive Quadratic Programming (SQP) method. New results are obtained for reactor length and optimal cost of the reactor. The effect of various top temperatures on the reactor performance is investigated and the simulation of ammonia reactor at each top temperature that provides further insight of the process has also been presented.

Keywords: Ammonia synthesis reactor, Optimal reactor length, SQP.

التصميم الامثل لمفاعل انتاج الامونيا

الخلاصة

يتضمن هذا البحث التصميم الامثل لمفاعل انتاج الامونيا باستخدام عملية الاستمثال للحصول على افضل موديل رياضي يمكن تطبيقه برصانه كبيرة من اجل وصف اداء عمل المفاعل بدقة عالية في عمليات التصميم والتشغيل والسيطرة. الهدف الرئيسي في مثل هذه المفاعلات هو تقييم افضل طول للمفاعل للوصول الى اعظم ربحية ناتجة من مفاعل انتاج الامونيا عند افضل درجة حرارة في اعلى المفاعل بحيث تلبي جميع شروط التفاعل. عُوملت عملية النمذجة والمحاكاة والاستمثال على اساس البرمجة غير الخطية باستخدام طريقة حل Successive Quadratic Programming (SQP) ذات الدقة العالية ضمن برنامج ال gPROMS وتم الحصول على ربحية اعلى من الربحية المستحصل عليها في الدراسات السابقة لمثل هذا النوع من المفاعلات. اضافة الى ذلك، تم دراسة تأثير عدة درجات حرارية في اعلى المفاعل على سلوك المفاعل ومناقشة النتائج المستحصل عليها من عملية المحاكاة.

الكلمات الدالة: مفاعل الامونيا، الاستمثال، النمذجة، المحاكاة.

Nomenclature

C_{pf} : Heat capacity of feed gas (kcal/kg.K).
C_{pg} : Heat capacity of reacting gas (kcal/kg.K).
f : Catalyst activity.
$f(Z)$: Objective function ($/year).
K_1, K_2 : Rate constants.
N_{N2} : Mass flow of nitrogen per unit area of catalyst zone (kg moles/m^2.hr).
P_{H2} : Partial pressures of hydrogen.
P_{N2} : Partial pressures of nitrogen.
P_{NH3} : Partial pressures of ammonia.
R : Gas constant.

T_r : Reference temperature (K).
U : Overall heat transfer coefficient (kcal/hr.m^2.K).
z : Reactor length (m).
ΔH : Heat of reaction (kcal/kg mole of N_2).
S_1 : Surface area of cooling tubes per unit length of reactor (m).
S_2 : Cross-sectional area of catalyst zone (m^2).
T_f : Feed gas temperature (K).
T_g : Reacting gas temperature (K).

Introduction

The treatment of chemical industrial problems has received considerable attention to many authors in such area, which can be classified as a control and design problems. In chemical engineering, the solution of the design problems would expect the most useful results rather than the control problems[1]. Among these problems, the optimal design of ammonia reactor.

Ammonia is regarded one of the most important commodity in chemical engineering operations. It is widely used as a raw material in process industries for production of different chemicals and products, mainly fertilizers, explosive materials, polymers, acids, coolers, fibers, plastics, refrigeration, pharmaceuticals, pulp paper, mining, metallurgy, and cleaning[2-6].

Ammonia is produced by an exothermic reversible reaction of hydrogen with nitrogen at high temperature and pressures according to the following reaction in the existence of catalyst:

$$N_2 + 3H_2 \Leftrightarrow 2NH_3$$

Such reaction is carried out in an important unit of ammonia plant, which is *ammonia synthesis reactor*[7]. The synthesis reactor is treated as a separate unit with the object of understanding its behavior and getting the key variables, which lead to its stable, sustained optimum operation. The reactor performance predicting are interested namely when changes are made in the controllable variables of the reactor with studying the variation of ammonia production as a result of the changes[3]. Since the first industrial production started in 1925, major changes have taken place in the design of ammonia synthesis reactors. Most of these changes were based on historical plant data rather than the chemical process itself in the reactors. Therefore, modeling, simulation and optimization studies have been built up via several investigators for different types of ammonia synthesis reactors, which made it necessary to have a mathematical description of the process[8,9].

Ammonia production depends on the feed gas temperature at the top of the reactor, the partial pressures of the reactants and the reactor length. The optimal design problem needs to get the optimal reactor length with maximum economic returns corresponding to the different top temperatures[2].

There are several studies that are interested in the modeling of ammonia reactor in the past, but all require some corrections owing to either uncorrected model employed or uncorrected algorithm. The main focus in this paper is therefore to find the optimal design of ammonia synthesis reactor and objective function of the system's subject to a number of equality and inequality constraints utilizing an alternative approach for describing the reactor operating conditions as accurately as possible. The optimization problem is posed as a Non-Linear Programming problem and is solved using a Successive Quadratic Programming (SQP) method (which is regarded to be one of the most promising approaches for solving constrained nonlinear optimization problem in addition to its successful application to many engineering optimization problems with high accuracy[10]) within gPROMS (**g**eneral **PRO**cess **M**odelling **S**ystem) software.

Methodology

In a typical ammonia reactor, the feed gas with nitrogen (21.75 mole %), hydrogen (65.25 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 production of ammonia depends on the temperature of feed gas at the top of the reactor (called as top temperature), the partial pressures of the reactants (nitrogen and hydrogen), and the reactor length. 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[1,4]. Figure 1 shows the schematic diagram of the ammonia reactor presented in this study[4].

Mathematical Model of Ammonia Synthesis Reactor

A mathematical model is a set of variables and a set of equations that build relationships among the variables to describe some aspects of the performance of the system under investigation. Process models are very profitable and have been used for operator training, safety systems design, design of operation in addition to design of operational control systems. The development of faster computers and advanced numerical methods has enabled modelling and solution of the whole process[11].

In the present study, a mathematical model is developed to obtain the optimal design of an ammonia synthesis reactor using SQP approach within gPROMS software (advanced languages and formalisms for model improvement, which allow the description of difficult differential and algebraic models and has several features that make it an attractive tool and suitable for the modelling, simulation and optimization of any plant process). The optimization problem consists of maximizing the economic profit subject to a number of equality and inequality constraints and based on energy and mass balance of the governing reactions related to ordinary differential equations (ODE's). The reactor length (z) is considered as an independent variable and mass flow rate of nitrogen (N_{N2}), feed gas temperature (T_f) and reaction gas temperature (T_g) of the mixture at the exit of the reactor are regarded as the dependent variables related to each other in addition to the reactor length through the above mentioned constraints. The following assumptions were used to create the mathematical model of the ammonia synthesis reactor[4,12]: (a) Longitudinal heat and mass transfer can be ignored, (b) The rate expression is valid, (c) The pressure drop across the reactor is negligible in comparison with the total pressure in the system, (d) The heat capacities of the reacting gas and feed gas are constant, (e) The gas temperature in the catalytic zone is the same catalyst particle temperature, and (f) The catalytic activity is uniform along the reactor and equal to unity.

Equality constraints

The ammonia reactor model includes mass and energy balance equations. Firstly, the increase in the feed gas temperature, as it goes up the reactor must be according to the heat gained from the reaction gas. Thereafter, the change in the temperature of reaction gas must be according to the heat lost to the feed gas in addition to the heat generated in the reaction. The mass balance equation can be written as follows[3]:

$$\frac{dN_{N_2}}{dz} = -f\left[k_1 \frac{p_{N_2} p_{H_2}^{1.5}}{p_{NH_3}} - k_2 \frac{p_{NH_3}}{p_{H_2}^{1.5}}\right] \text{...(1)}$$

The partial pressures appearing in the above equation are described as follows[3,13]:

$$p_{N_2} = \frac{286 N_{N_2}}{\left(2.598 N_{N_2} + 2N_{N_2}\right)} \text{.........(2)}$$

$$p_{H_2} = \frac{3\left(286 N_{N_2}\right)}{\left(2.598 N_{N_2} + 2N_{N_2}\right)} \text{...........(3)}$$

$$p_{NH_3} = \frac{286\left(2.23 N_{N_2}^0 - 2N_{N_2}\right)}{\left(2.598 N_{N_2}^0 + 2N_{N_2}\right)} \text{.......(4)}$$

Whereas the reaction rate constants can be stated as[2,4,13]:

$$k_1 = 1.78954 \times 10^4 \exp\left(\frac{-20800}{R\,T_G}\right) \text{...(5)}$$

$$k_2 = 2 \cdot 5714 \times 10^{16} \exp\left(\frac{-47400}{R\,T_G}\right) \text{...(6)}$$

The energy balance equation that need to be satisfied to obtain the value of the feed and reacting gas temperature, are[1-4]:

$$\frac{dT_f}{dz} = -\frac{US_1}{WC_{pf}}\left(T_g - T_f\right) \text{.............(7)}$$

$$\frac{dT_g}{dz} = -\frac{US_1}{WC_{pg}}\left(T_g - T_f\right) + \frac{(-\Delta H)S_2}{WC_{pg}}(f)\left(-\frac{dN_{N_2}}{dz}\right) \text{...........(8)}$$

Since the mathematical model presented above consists of a set of differential equations along the reactor length, it is necessary to define boundary conditions, which are as follows [3,4]:

$$T_f(z=0) = T_r \text{........................(9)}$$

$$T_g(z=0) = T_f \text{........................(10)}$$

$$N_{N_2}^0(z=0) = 701.2\, kmol/m^2hr \text{.....(11)}$$

Inequality constraints

The upper and lower bounds of the design variables are given as follows[2-4, 13]:

$$0.0\, kmol/m^2hr \le N_{N_2} \le 3220\, kmol/m^2hr \text{............(12)}$$

$$400\,K \le T_f \le 800\,K \text{...............(13)}$$

$$0.0\,m \le z \le 10.0\,m \text{..........(14)}$$

Since the reaction gas temperature (T_g) depends on the nitrogen mass flow rate (N_{N2}), feed gas temperature (T_f) and reactor length (z), there is no need to implicate any boundaries on T_g. From the mathematical model presented above, the degrees of freedom equal to one. Thus, the reactor length will be specified for this purpose and the other variables are evaluated within the system model then pass these variables to the optimization routine.

Objective function

The objective function is the economic profit depending 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. Actually, a relation of this objective has been formulated by Murase et al[1] then the stated objective function was correct by Edgar and Himmelblau[12], and finally the objective function was modified by Upreti and Deb[13] to be:

$$f(z, N_{N_2}, T_g, T_f) = f(Z) = 1.33563\times10^7 - 1.70843\times10^4 N_{N_2} + 704.09(T_g - T_r) - 699.27(T_f - T_r) - \begin{pmatrix} 3.45663\times10^7 + \\ 1.98365\times10^9 z \end{pmatrix}^{0.5} \quad ..(15)$$

It is clearly noticed from the above equation that the objective function depends mainly on four variables: the reactor length z, nitrogen proportion N_{N2}, the reacting gas temperature T_g, and the feed gas temperature T_f, for a given top temperature T_r.

Optimization problem formulation

The optimal design problem requires obtaining the optimal reactor length giving maximum economic profits from the reactor operation corresponding to different top temperatures.

Mathematically, the optimization problem can be described as:

$$\max_{T_f,\, z,\, N_{N2}} \quad f(Z)$$

$$s.t \quad f(z, x(z), \dot{x}(z), u(z), v), \quad [z_0, z_f]$$

$$T_{f_L} \le T_f \le T_{f_U}$$

$$z_L \le z \le z_U$$

$$N_{N2L} \le N_{N2} \le N_{N2U}$$

The model equations, which can be written in compact form as: $(f(z, x(z), \dot{x}(z), u(z), v) = 0, [z_0, z_f])$, where z is the independent variable (length of the reactor), $x(z)$ gives the set of all differential and algebraic variables, $\dot{x}(z)$ denotes the derivative of differential variables with respect to length of the reactor, $u(z)$ is the control variables, and v represents the design variables (length independent constant parameters). The length interval of interest is $[z_0, z_f]$ and the function f: is assumed to be continuously differentiable with respect to all its arguments[14]. L and U is the lower and upper bounds, respectively. The optimization solution method used by gPROMS is a two-steps method known as feasible path approach. The first step performs the simulation to converge all the equality constraints and to satisfy the inequality constraints and the second step performs the optimization (updates the values of the optimization parameters).

Results and Discussion

Here, the modelling, simulation and optimization process has been carried out by using gPROMS software. The optimization problem based on a Non-Linear Programming (NLP) problem and is solved using Successive Quadratic Programming (SQP) method.

The effect of the top temperature T_r on the optimal reactor length has been studied in this work. For each value of T_r, the optimization algorithm to maximize the objective function is evaluated and an optimal reactor length is obtained subject to the process constraints. The values of constant parameters used in this work are listed in Table 1[1,3,4].

Optimization results

Upreti and Deb[13] reported that the differential equations will be unstable at the top temperature (T_r) above 706K and there will be reverse reaction below 664K. Therefore, the effect of T_r on the reactor performance has been studied over the range mentioned above (i.e. below 664K and above 706K). The optimal parameters obtained at each T_r are shown in Tables (2-7). As can be seen from these Tables, the optimal value of the reactor length with satisfying all the inequality constraints is achieved at the top temperature of 694K with the reactor length 5.7132m and maximum objective function (ammonia profit) 6.0667×10^6 \$/Year compared with other top temperatures. Where below 664K (such as 600 and 650K) and above this top temperature (such as 706, 750 and 800K), the reactor length is obtained with the maximum ammonia profit lower than this obtained at 694K, which indicates that the best top temperature for the ammonia synthesis reactor should be carried out at the temperature of 694K.

Table 8 shows the comparison results obtained from this study and those obtained by previous studies. It is clearly observed from this Table that the new approach (SQP) used in this work to maximize the ammonia profit is better than the methods used with all previous works (that used different solution methods for maximizing the objective function to get the optimal design of ammonia synthesis reactor) in this field. This new result can be attributed to the SQP approach utilized in this study (has high accuracy in evaluating the control variables of the process) within gPROMS package. Furthermore, this approach is a highly trusted method for solution of such mathematical models. Thus, the correct optimum reactor length can be considered as 5.7132m with an objective function value of 6.0667×10^6 \$/year.

Profiles of temperature and flow rate

In order to describe the performance of the ammonia reactor, the simulation of such reactor is necessary. This performance has been carried out at each top temperature, where the objective function (ammonia profit), the feed gas temperature T_f, the reacting gas temperature T_g and the nitrogen flow rate N_{N2} are plotted along reactor length with a marker of the optimal values at each top temperature as shown in Figures 2-7. These Figures showed that the objective function increases with reactor length. Continuing with the points reported by Upreti and Deb[13], it is has been noted from Figures 3, 4, 6 and 7 that the profiles are smooth and there are no spikes are founded as mentioned by Upreti and Deb[13]. However, the step size employed for solving the mathematical model in this study was set to 0.001 to make sure that the profiles are smooth and there are no spikes in addition to make sure that no spikes were missed. But even at this small step size, the profiles are very smooth and the equations are not unstable even at a top temperature higher than 706K. Furthermore, there is no reverse reaction predominated the forward reaction at the top temperature even below 664K as reported by Upreti and Deb[13], where such trend was observed in the profiles obtained. These trends were noticed due to the incorrect equations used by Upreti and Deb[13] or could be attributed to the used NAG library's subroutine (which is D02EBF), but neither spikes nor reverse reaction effect were founded in this study.

Conclusions

An optimal design of ammonia synthesis reactor is investigated here. It has been modelled as a system of differential–algebraic equations within gPROMS Model Builder. An optimization framework has been developed to tackle the optimal design and operation problem of ammonia reactor. The optimization problem formulation has been presented to give maximum economic of ammonia production. It has been carried out using a new alternative approach (the optimization problem was posed as a Non-linear programming (NLP) problem and was solved using a SQP method within gPROMS software). An accurate process model for ammonia reactor is very important to accurately model the process, so that the model can be effectively used for simulation, optimization and control.

Depending on the results obtained from this study, it can be concluded that the best top temperature obtained is 694K to satisfy the inequality constraints (where the optimum reactor length depends upon the top temperature). Also, results showed that the profiles of temperatures and flow rate are very smooth and there is neither spikes nor reverse reaction impact. In further, all the model equations were stable even at the top temperature as high as 800K. Finally, SQP method has been demonstrated to be able to give accurate results of reactor length 5.7132m with corresponding ammonia profit of 6.0667×10^6 \$/year and gave better objective function in comparison with those obtained by previous studies.

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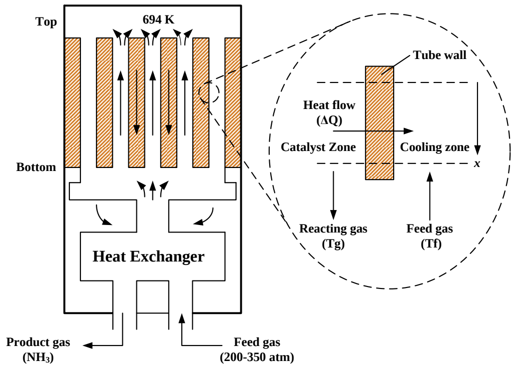

Figure (1) Configuration of an ammonia synthesis reactor

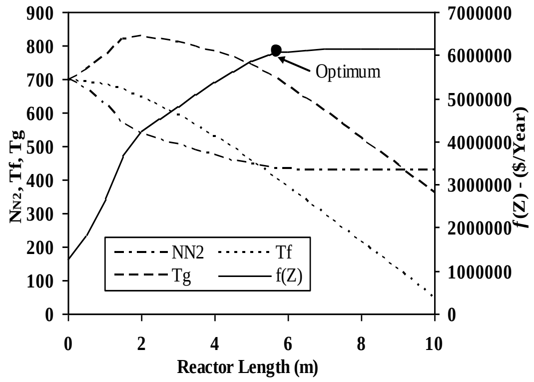

Figure (2) Parameters profile and ammonia profit along the reactor length at T_r = 694 K

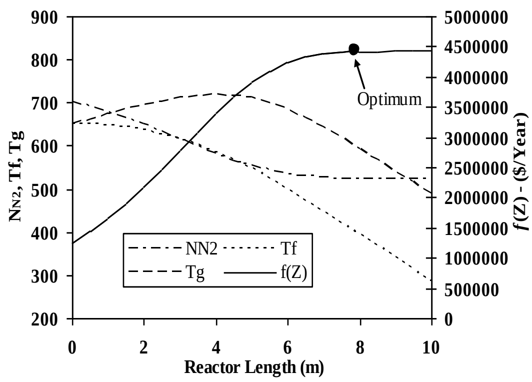

Figure (3) Parameters profile and ammonia profit along the reactor length at T_r = 650 K

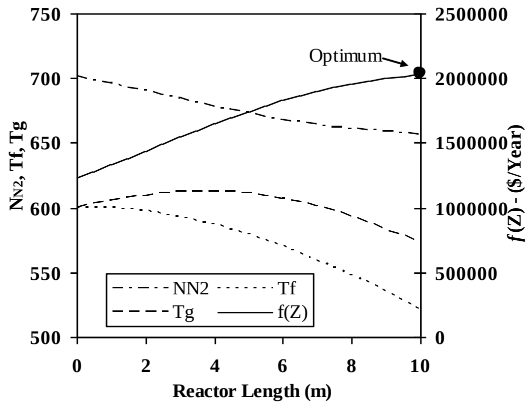

Figure (4) Parameters profile and ammonia profit along the reactor length at T_r = 600 K

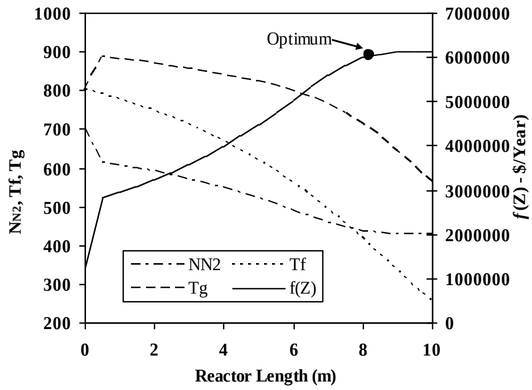

Figure (7) Parameters profile and ammonia profit along the reactor length at T_r = 800 K

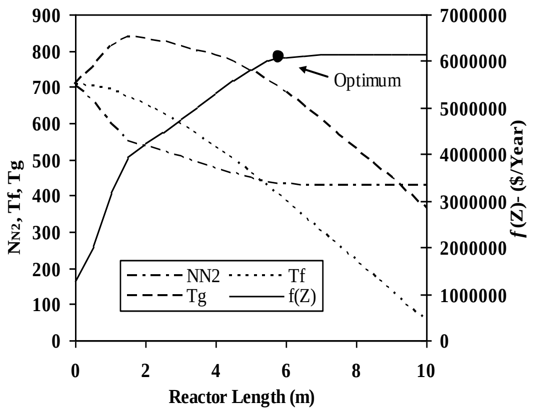

Figure (5) Parameters profile and ammonia profit along the reactor length at T_r = 706 K

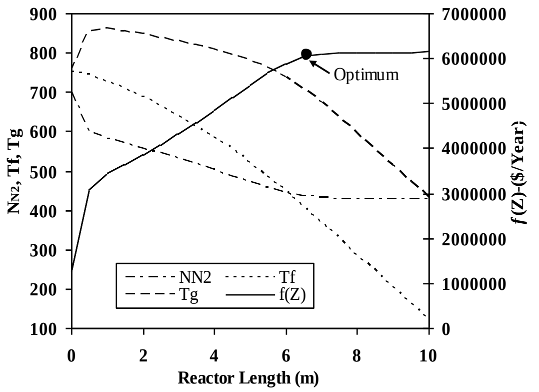

Figure (6) Parameters profile and ammonia profit along the reactor length at T_r = 750 K

Table (1) Values of parameters used in this work

Parameter	Values
U	500 kcal/hr.m^2.K
S_1	10 m
S_2	0.78 m^2
C_{pf}	0.707 kcal/kg.K
C_{pg}	0.719 kcal/kg.K
W	26400 kg/hr
ΔH	-26600 kcal/kg mole of N_2
R	1.987 kcal/kg mol.K
f	1

Table (2) Optimal parameters obtained at T_r = 694 K

Parameter	Optimal value
Z	5.7132 m
f(Z)	6.0667 × 10^6 $/Year
Tf	400.559 K
Tg	698.989 K
N_{N2}	432.658 kg mol/m^2.hr

Table (3) Optimal parameters obtained at T_r = 650 K

Parameter	Optimal value
Z	7.8812 m
f(Z)	4.4282 × 10^6 $/Year
Tf	400.206 K
Tg	598.741 K
N_{N2}	523.382 kg mol/m^2.hr

Table (4) Optimal parameters obtained at T_r = 600 K

Parameter	Optimal value
Z	10.0 m
f (Z)	2.0316 × 10^6 \$/Year
Tf	521.968 K
Tg	571.941 K
N_{N2}	656.673 kg mol/m^2.hr

Table (5) Optimal parameters obtained at T_r = 706 K

Parameter	Optimal value
Z	5.7889 m
f (Z)	6.0659 × 10^6 \$/Year
Tf	400.201 K
Tg	698.822 K
N_{N2}	432.671 kg mol/m^2.hr

Table (6) Optimal parameters obtained at T_r = 750 K

Parameter	Optimal value
Z	6.5950 m
f (Z)	6.0544 × 10^6 \$/Year
Tf	400.225 K
Tg	699.299 K
N_{N2}	432.929 kg mol/m^2.hr

Table (7) Optimal parameters obtained at T_r = 800 K

Parameter	Optimal value
Z	8.1996 m
f (Z)	6.0364 × 10^6 \$/Year
Tf	400.174 K
Tg	699.773 K
N_{N2}	433.212 kg mol/m^2.hr

Table (8) Comparison results between this study and previous studies

Authors	Solution method	Optimum reactor length (m)	Objective function (Ammonia profit (10^6 \$/Year))
Murase et al.[1]	PMP	5.18	Not mentioned
Edgae & Himmelblau[12]	LGRG	2.58	1.29
Upreti & Deb[13]	D02EBF with GA	5.33	4.23
Babu et al.[15]	GEAR with DE RKVS with DE	6.79 7.16	4.84 4.84
Babu & Angira[2]	D02EJF with QN	6.586	5.0
Yusup Yew et al.[4]	Shooting Methods	6.695	5.015
Ksasy et al.[3]	ODE45 with GA	6.4253	5.6635
This study	SQP	5.7132	6.0667