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PROCESS SIMULATION OF AMMONIA SYNTHESIS FOR INCREASING HEAT RECOVERY IN A THERMAL STORAGE PLANT: A REVIEW

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Abstract

Thermal storage of solar energy can be achieved in solids and liquids, during solar insolence, for subsequent recovery to enable 24-hour base-load plant operation similar to conventional fossil-fueled and nuclear power plants. Liquid ammonia, due to its global availability and chemical suitability, has been considered for thermal energy storage in plants of the order of 10 MW(e). The energy is stored in chemical bonds of constituent gases arising from the endothermic dissociation of ammonia, and subsequently recovered in the well-known exothermic synthesis Haber-Bosch reaction.

The efficiency of such a solar plant depends on the process variables – temperature, pressure and flow-rate; which can be modeled with the thermo-fluid conservation equations incorporating the underlying thermodynamics and chemical reaction kinetics. This paper reviews the models, and the computational schemes, that have been used to simulate the industrial ammonia synthesis process. We have also reviewed the accuracy of the simulations reported in the literature.

Keywords Solar Thermal Storage, Ammonia Synthesis, Solar Heat Recovery, Optimization of Synthesis Process.

Introduction

Solar energy currently accounts for an installed capacity of about 23 GWe, compared with geothermal (installed capacity 10.7 GW), and wind (160 GW) [1]. This is insignificant in the global scenario where in 2010, the total primary energy consumption was 12002.4MTOE[**][1]consisting of oil (33.8%), coal (29.6%), natural gas (23.8%), hydroelectric (6.5%) and nuclear (5.6%). Even though renewable sources such as solar, geothermal and wind are not presently significant, they offer the promise of providing clean and sustainable energy by mitigating the effect of the carbon release from fossil fuels, in the form of greenhouse gases [1, 2]. Such reductions are necessary for the environment and are binding on states signatory to the Kyoto Protocol [46]. Emission of greenhouse gases (carbon dioxide, methane, nitrous oxide, hydrofluorocarbons, perfluorocarbons and sulphur hexafluoride) as well as toxic and pollutant gases, also have a harmful effect on people.

The Sun, as the primary source of energy for the solar system, supplies over 30,000 TWyr/yr which, compared with the global energy requirement of the order of 20 TWyr/yr may be considered to be virtually inexhaustible source. The issues which will ensure its place in the future energy scenario are its economic competitiveness in comparison with existing technologies. A key technological issue that lies at the core of economic competitiveness of solar energy is the operation of solar energy power plants. Presently, solar power plants, based on photovoltaic (PV) and concentrated solar power (CSP)

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[**] MTOE=million tonnes oil equivalent: 1 TOE is approximately equal to 42 GJ heat units, or 12 MWh electricity

technologies [16, 19], are capable of electricity generation during solar insolence only. Continuous, base-load operation will only be possible if such plants can generate electricity in the absence of solar insolence; and hence thermal storage mechanism becomes necessary.

The thermal energy storage technologies can be classified [29] by the mechanism of heat *viz* (i) sensible, (ii)latent, (iii) sorptive, and (iv) chemical. In the sensible heat storage systems, there is the possibility of liquid (water tank, aquifier, thermal oil) and solid systems (building mass, concrete, ground). In the latent heat storage systems, both organic (parrafins) and inorganic (hydrate salts) compounds can be used. In the sorptive, both absorption and adsorption systems can be used. Finally, in the chemical storage, energy can be stored in chemical bonds which can be broken endothermically and recovered in a synthesis exothermically. Storage materials and technology will also depend on the temperatures in the plant [27].

A base-load plant of 10 MW(e), assuming that a solar insolation of 1 kW/m^2 is available for 8 hours in a day (28.8 MJ/m^2, compared with 20 MJ/m^2 for Pakistan [57] would require 400 parabolic dishes, each of area 400 m^2 [41], with a synthesis plant of 1500 MeT per day.

The Synthesis Process

The Haber-Bosch process, first demonstrated by Fritz Haber in 1909 and scaled up to an industrial process by Carl Bosch in 1913. Both Haber and Bosch were awarded Nobel Prizes for their inventions, and ammonia was used in Germany in the First World War for the manufacture of explosives.

Ammonia Industry

Global fertilizer industry produces about 170 million tones of fertilizer nutrients every year [18] for boosting agricultural output, of which more than 15 million tones was ammonia produced in 2009. Fertilizers are based on nitrogen, phosphorus or potassium. Nitrogen accounts for 78% of the earth's atmosphere. Since plants can not breathe nitrogen, it must be converted to a suitable form such as ammonia. Its major uses are as fertilizer and for production of nitrogen containing compounds such as nitric acid. It is also used as a refrigerant and in textile processing. Ammonia (NH_3) stays in the liquid form at temperatures higher than its melting point -77.73 ^oC and has a density of 681.9 kg/m^3 at its boiling point -33.34 ^oC; it must thus be kept at very low temperature or stored at very high pressure. Liquid ammonia was first produced on an industrial scale in Germany, during the First World War, by the Haber-Bosch Process. In industry, the Haber-Bosch process, involving the steam reforming of methane to produce hydrogen is used with nitrogen taken from the air, to produce ammonia. The typical size of urea plants is 1000 MeT per day with a capital cost of US$ 150 million. The total production of ammonia was 130 million tones in 2000, produced in 80 countries and 85% of which was used for nitrogen fertilizer production [39]. The largest chemical industry in the world is in the U.S. [40], with ammonia being the most important intermediate chemical compound produced in 41 plants. In Pakistan, there are eight urea fertilizer plants with a large ammonia plant capacity [9].

Ammonia Dissociation and Synthesis

The dissociation of ammonia $2NH_3 \Leftrightarrow N_2 + 3H_2$ (ΔH = 66.9 kJ/mol) is an endothermic reaction that can be carried out by thermo-catalytic decomposition using catalysts: ruthenium, indium, nickel, Fe-Al-L, Fe-Cr. Typical temperatures are in the range of 850 – 1000 ^oC. Approximately 1.4 kW power per cubic meter of hydrogen is typically used. Conversely, the synthesis of ammonia from nitrogen and hydrogen reactant gases $N_2 + 3H_2 \Leftrightarrow 2NH_3$ (ΔH = -92.22 kJ/mol) is an exothermic reaction for which the pressure required is in the range 130 – 250 bar, and the temperature required is in the range 250 – 600 ^oC. High temperature gives higher reaction rate, but as reaction is exothermic, higher temperature according to Le Chatelier's principle causes the reaction to move in the reverse direction hence a reduction in product. Similarly, higher Temperature reduces the equilibrium constant and hence the amount of product decreases; this is the Van't Hoff equation: $\ln K = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$. An increase in pressure, however, causes a forward reaction and is thus favorable. Synthesis is achieved by using catalysts such as osmium, ruthenium, and iron-based catalysts.

Ammonia Synthesis Plant

The principle of circulating gas over the catalyst in a loop system, first appreciated by Haber in 1908, is still an important feature of modern ammonia plants. Over the past 50 years the typical operating pressures with available catalysts have been in the range 120 – 350 bar (1740 – 5075 psi). However during the last 20 years low pressure synthesis loops operating in the region of 80 - 120 bar (1160 - 1740 psi) have been an integral part of new technology. Figure 1 below shows a synthesis loop for a typical 1500 TPD plant operating at 200 bar (2900 psi) and using a three bed radial converter.

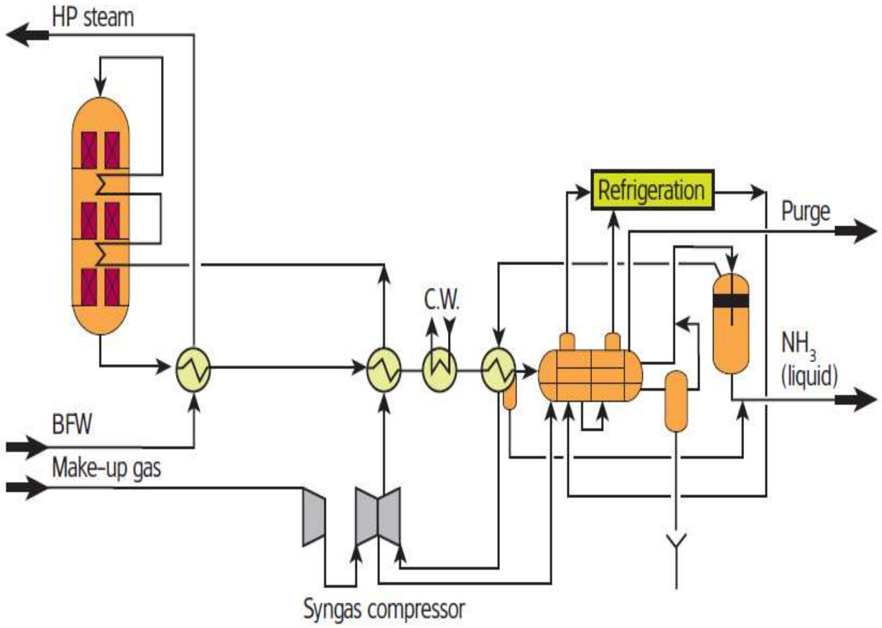


Figure 2. Ammonia loop for typical 1500 TPD plant

The ammonia synthesis technology is now mature, with the market dominated by five licensers-Haldor Topsøe, M.W. Kellogg, Uhde, ICI, and Brown & Root, of which Haldor Topsøe has a 50 per cent world market share as supplier of the technology [3, 4, 5, 6, 7,12, 13, 15, 39]. Figure 2 shows Udhe Dual Pressure Process, based on using a once-through converter to produce some ammonia before entering the conventional synthesis loop.

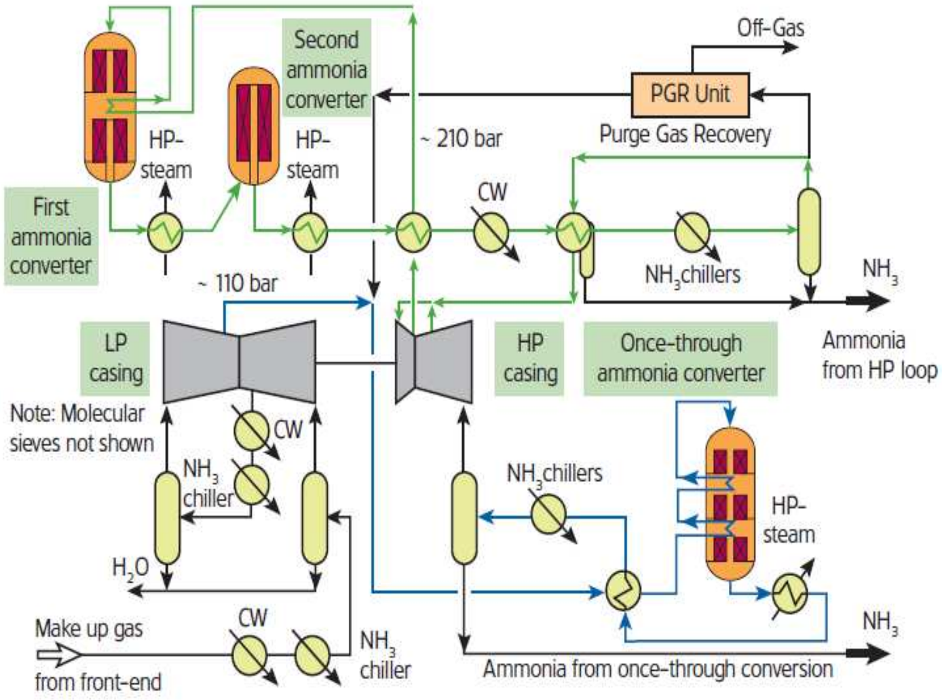


Figure 2. Uhde Dual Pressure Process – ammonia synthesis loop

A simplified Thermal Storage Plant (TSP) model [43] using such as reactor, shown in Figure 3, is considered as it includes the essential features of an ammonia synthesis plant. The input syn gas stream (ST1), consisting of nitrogen, hydrogen and small amounts of other gases, is taken from the day-cycle ammonia dissociation of the solar plant [42]. This feed-stream is compressed to the temperature and higher pressure required for synthesis, typically, of the order of 250 -600 ^{o}C and 130 - 250 bar. This stream is then mixed with the recycle stream (ST10) and fed into the catalyst-containing synthesis reactor where the synthesis reaction, $N_2 + 3H_2 \Leftrightarrow 2NH_3$ in the forward direction, converts nitrogen and hydrogen into ammonia producing energy. The effluent stream passes through the recovery heat exchanger and liquid ammonia condenser E-1 and into the Knock-Out drum F-1, where the liquid ammonia is sent to the storage tank and stream ST6 is carried to the purging system for removing inert gases which are 'poisons' for the catalyst in the reactor. Another re-cycle compressor is required at this stage to restore the pressure to the required level till the stream (ST10) is mixed with the feed stream and enters as stream ST3.

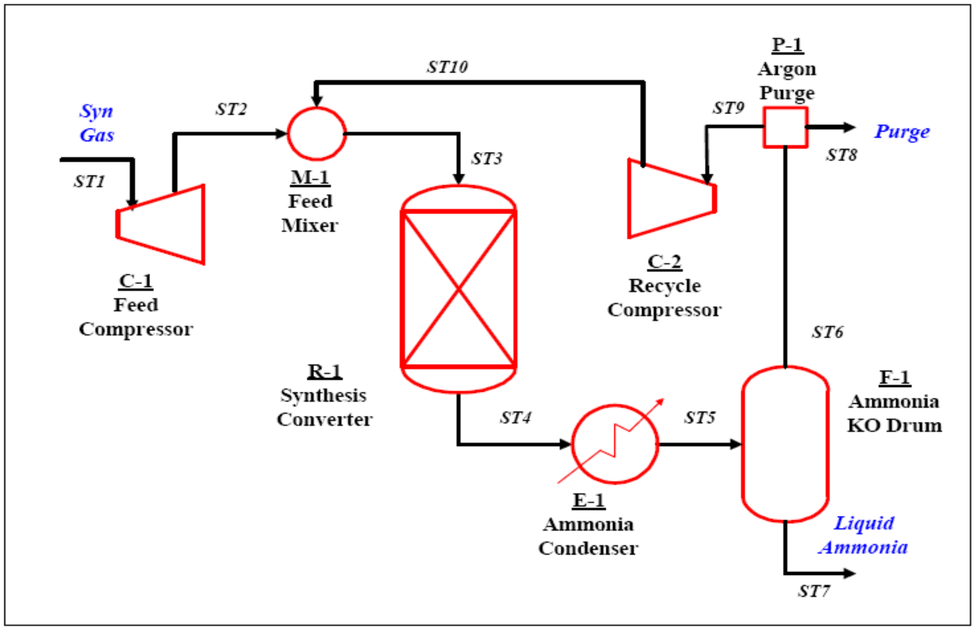


Figure 3. Ammonia synthesis energy recovery system for a Thermal Storage Plant.

Review of Mathematical Models

The synthesis of ammonia from the flow of syn gases in the convertor can be modeled using the laws of conservation of mass, momentum and energy for non-isothermal multi-component systems undergoing chemical reactions and mass transfer [35]. In the case of unsteady flow the governing equations are

Mass:

$$\frac{d}{dt}m_{tot} = \Sigma\omega_1 - \Sigma\omega_2 + \omega_0 = \Sigma\rho_2\langle\upsilon_2\rangle S_2 + \omega_0 \qquad (1)$$

Mass of Species α:

$$\frac{d}{dt}m_{\alpha,tot} = \Sigma\omega_{\alpha 1} - \Sigma\omega_{\alpha 2} + \omega_{\alpha 0} + r_{\alpha,tot} \qquad \alpha = 1,2,3,......N \qquad (2)$$

Momentum:

$$\frac{d}{dt}P_{tot} = \Sigma(\frac{\langle\upsilon_1^2\rangle}{\langle\upsilon_1\rangle}\omega_1 + p_1S_1)u_1 - \Sigma(\frac{\langle\upsilon_2^2\rangle}{\langle\upsilon_2\rangle}\omega_2 + p_2S_2)u_2 + m_{tot}g + F_0 - F_{f\to s} \qquad (3)$$

(Total) energy:

$$\frac{d}{dt}(K_{tot} + \Phi_{tot} + U_{tot}) = \Sigma(\frac{1}{2}\frac{\langle\upsilon_1^3\rangle}{\langle\upsilon_1\rangle} + gh_1 + \hat{H}_1)\omega_1 - \Sigma(\frac{1}{2}\frac{\langle\upsilon_2^3\rangle}{\langle\upsilon_2\rangle} + gh_2 + \hat{H}_2)\omega_2 + W_m + Q_0 - Q \qquad (4)$$

where

m	mass	Φ	potential energy
ω	mass flow rate	U	internal energy
r	molar production	H	enthalpy per unit mass
P	linear momentum	Q	heat
υ	velocity vector	W	work
F	force (external, fluid to solid)	S	surface area
K	kinetic energy		

In terms of molar quantities, the continuity equation is expressed in terms of the molar concentration c, and the mole fractions x_i as

$$c\left(\frac{\partial x_\alpha}{\partial t} + (v^* \cdot \nabla x_\alpha)\right) = -(\nabla \cdot J^*_\alpha) + R_\alpha - x_\alpha \sum_{\beta=1}^{N} R_\beta \qquad \alpha = 1,2,3,.....N \tag{5}$$

Table 1: Equations of change of Multi-component Mixtures in terms of the Molecular Fluxes

Total mass:	$\frac{D\rho}{Dt} = -\rho(\nabla \cdot v)$
Species mass: (α=1,2,3,…..N)	$\rho \frac{D\omega_\alpha}{Dt} = -(\nabla \cdot j_\alpha) + r_\alpha$
Momentum:	$\rho \frac{Dv}{Dt} = -\nabla \rho - [\nabla \cdot \tau] + \rho g$
Energy:	$\rho \frac{D}{Dt}(\hat{U} + \frac{1}{2}v^2) = -(\nabla \cdot q) - (\nabla \cdot pv) - (\nabla \cdot [\tau \cdot v]) - (\rho v \cdot g)$

The above have been expressed by Dashti [25] as

$$\left\{ \begin{array}{c} \frac{dz}{dx} = \frac{\eta r_{NH_3}}{2F^o_{N_2} / A} \\ \rho u C_p \frac{dT}{dx} + (-\Delta H_r)\eta r_{NH_3} = 0 \\ \frac{dP}{dx} = -\mu \nabla^2 u = -150 \frac{(1-\varepsilon)^z}{\varepsilon^3} \times \frac{\mu u}{d_p^2} - 1.75 \frac{(1-\varepsilon)}{\varepsilon^3} \times \frac{\rho u^2}{dp} \end{array} \right\} \tag{6}$$

A simpler analysis ignores the pressure drop in flow reducing to the conservation equations for mass and energy with reaction kinetics, used by Yuguo [59] and Dashti [25]

$$\frac{dz}{dx} = \frac{\eta R_A}{2F_N^o / A} \qquad (7)$$

$$\rho u C_p \frac{dT}{dx} + (-\Delta H_r)\eta R_A = 0 \qquad (8)$$

For the reaction kinetics, the Temkin-Pyzhev [25,59] form of the synthesis reaction rate as a function of the pressure, temperature, and activities is used

$$R_A = 2k\left[K_a^2 a_N \frac{a_H^{1.5}}{a_A} - \frac{a_A}{a_H^{1.5}}\right] \qquad (9)$$

where the activities are defined as $a_i = y_i \phi_i P$. The individual activities are:

$$\phi_H = \exp\left\{e^{(-3.8402T^{0.129}+0.541)} P - e^{(-0.1263T^{0.5}-15.98)} P^2 + 300\left[e^{(-0.011901T-5.941)}\right] e^{-P/300}\right\} \qquad (10a)$$

$$\phi_N = 0.93431737 + 0.2028538\, X10^{-3} T + 0.295896\, X10^{-3} P - 0.270727\, X10^{-6} T^2 + 0.4775207\, X10^{-6} P^2$$

(10b)

$$\phi_A = 0.1438996 + 0.2028538 X10^{-2} T + 0.4487672 X10^{-3} P - 0.1142945 X10^{-5} T^2 + 0.2761216 X10^{-6} P^2$$

. (10c)

The Arrhenius rate form is given as

$$k = k_o \exp\left(-\frac{E}{RT}\right) \qquad (11)$$

The specific heat capacities of hydrogen, nitrogen, methane and argon of the syngas (T in Kelvin, C_p in J/mol-K) expressed as:

$$c_p H_2 = 4.184(6.952 - 0.04567E - 2T + 0.09563E - T^2 - 0.2079E - T^3)$$

$$c_p N_2 = 4.184(6.903 - 0.03753E - 2T + 0.01930E - 5T^2 - 0.6861E - 9T^3)$$

$$c_p CH_4 = 4.184(4.75 + 1.2E - 2T + 0.303E - 5T^2 - 2.63E - 9T^3) \qquad (12a)$$

$$c_P Ar = 4.184 * 4.9675$$

For ammonia, the Shomate equations [10],

$$c_P NH_3 = A + B*t + C*t^2 + D*t^3 + \frac{E}{t^2} \qquad (12b)$$

T in the range 298-1400 K,

$$t = \frac{T}{1000}$$

$$A = 19.99563; B = 49.77119; C = -15.37599; D = 1.921168; E = 0.189174$$

have been used for the temperature range of interest (500-800K) and compared with simplified expressions [37]:

$$\begin{aligned} c_P N_2 &= 27.27 + 4.93e - 3T \\ c_P H_2 &= 27.01 + 3.51e - 3T \qquad (12c) \\ c_P N_2 &= 29.75 + 25.11e - 3T \end{aligned}$$

For a compressor, the power requirements [37,50] for isentropic compression, are obtained as

$$W_s = \frac{\gamma}{\gamma - 1} R T_1 \left[1 - \left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} \right]. \qquad (13)$$

The actual work will of course be larger than W_s and the ratio W_s / W_{actual} will depend on the compressor efficiency. In terms of the initial and final temperatures, the work W_s can also be found from

$$W_s = -\Delta H = C_p (T_1 - T_2) \, . \qquad (14)$$

More generally, for a multi-stage compressor with *n* units, with the compression ratios (*r)* in all the stages equal, the total work can be estimated from

$$W_s = \frac{n\gamma}{\gamma - 1} R T_1 \left[1 - (r)^{(\gamma-1)/\gamma} \right]. \qquad (15)$$

where, for an ideal gas $P_1 V_1 = R T_1$. The above expressions are based on the assumption that specific heats remain constant in the pressure and temperature range. In this analysis, the compression power requirements for a single-stage reciprocating compressor are obtained.

Similar models are also used to determine the compression requirement for recycle in the converter, refrigeration duty, vaporizer and purge systems. Additional objectives will be to quantify process-variable trade-offs with an aim to progress towards an “optimal design”. Thus, an issue worth exploring is: what percentage change in the plant operating parameters can result in an incremental change in availability of syn gases which can be used to generate electricity at night from the NH_3 synthesis exothermic reaction.

The above model can be used to carry out an energy balance of the Process Flow Diagram (PFD). The ‘energy input’ components are thus the compressors (C-1 and C-2), and the refrigeration systems for condensing liquid ammonia (E-1), while the ‘energy output’ system is the heat recovery system with E-1 or taken separately.

The equilibrium constant is obtained from

$$\log K_a = -2.691122 \log T - 5.51925 X 10^{-5} T + 1.848863 X 10^{-7} T^2 + \frac{2001.6}{T} + 2.689 \, . \qquad (16)$$

The overall synthesis rate (kmol of ammonia produced per hr per unit volume of catalyst) is ηR_A where η is the catalyst effect factor [25]. It is defined as

$$\eta = b_o + b_1 T + b_2 Z + b_3 T^2 + b_4 Z^2 + b_5 T^3 + b_6 Z^3 \qquad (17)$$

and may have a significant effect on the overall efficiency.

The resulting equations are coupled non-linear partial differential equations, which are converted to ordinary differential equations and solved by numerical integration [51].

The above model has been used by Siddiq *et al* [11] to obtain the molar flow rates and temperature of the syngas in a single-bed catalyst convertor, and the net power produced by the TSP. For a plant of magnitude similar to that described in Dashti [25] the results for the nitrogen conversion, syngas temperature and molar flow rates are shown in Figs. 4-7.

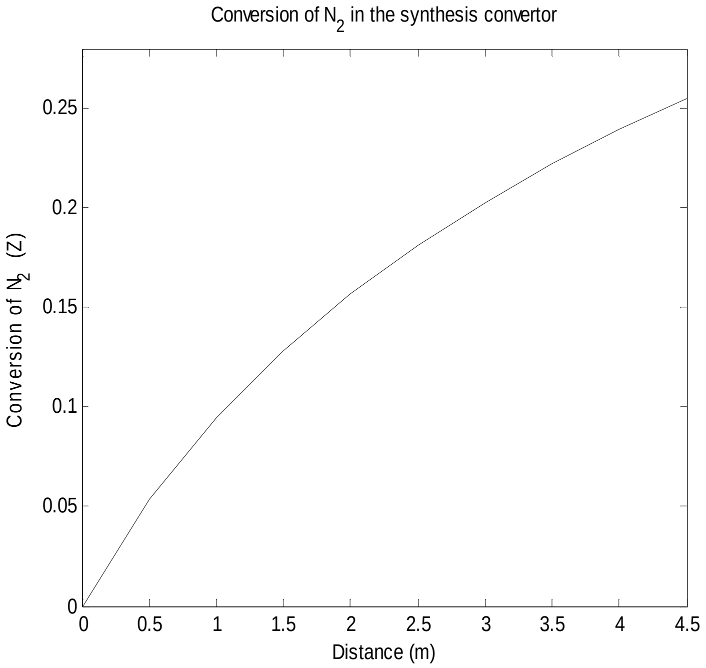


Figure 4. Conversion of Nitrogen along a single-bed catalyst

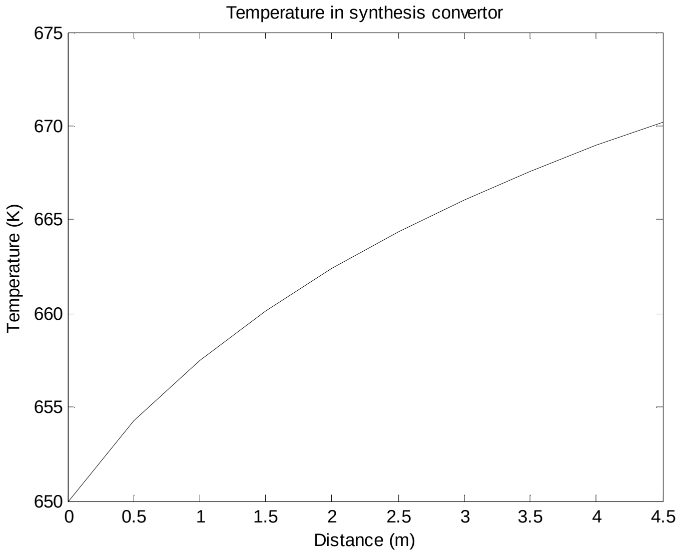


Figure 5. Syngas temperature in converter.

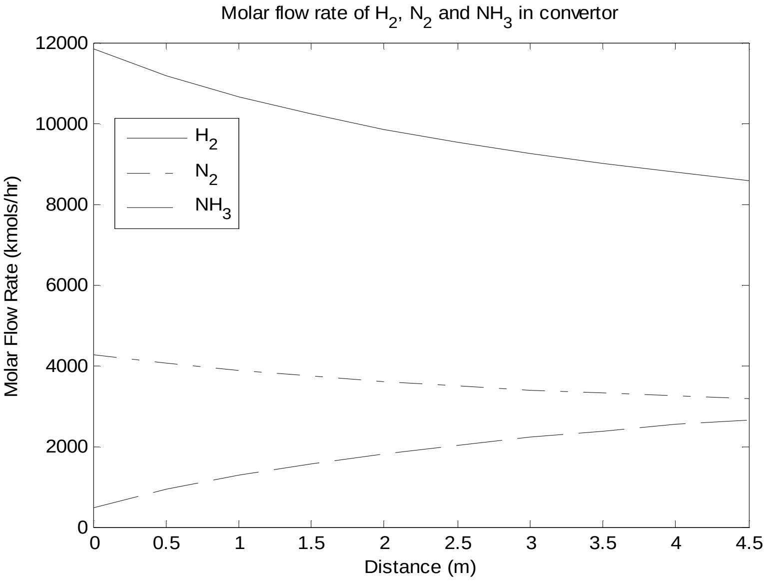


Figure 6. Molar flow rate in converter.

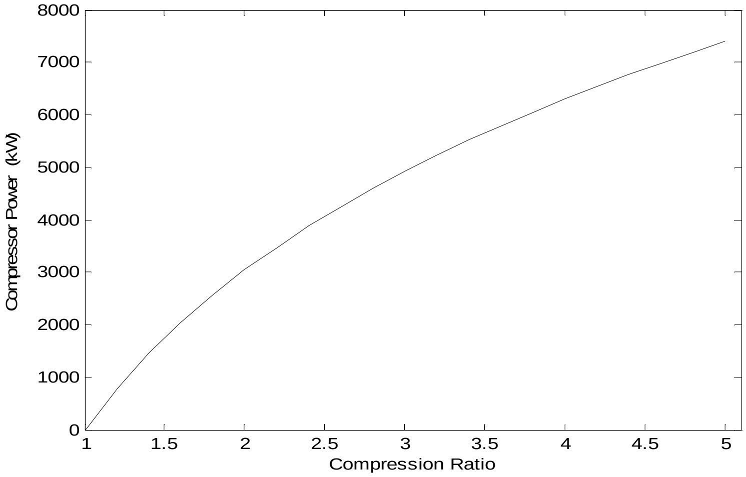


Figure 7. Syngas compression requirement.

It was found that the overall energy availability from the exothermic synthesis of ammonia is of the order of 32.4 MW(th), of which about 50% is available in the top 30% of the convertor. This energy availability was assessed in comparison with the syngas compression requirement shown in Figure 7. As shown, the compressor power is dependent on the syngas flow-rate, the compression ratio and the initial temperature. As a rough guide a compression ratio of 3, typical of industrial multistage compressors, would require of the order of 5 MW(e). The two dominating energy factors of a thermal storage plant based on the endothermic dissociation and exothermic synthesis of ammonia were quantified. It was determined that the syngas compression may greatly exceed the useful work realizable from such a plant. Factors to investigate in greater detail include the hydrogen/nitrogen ratio, the purge gas ratio, the ammonia content of the convertor feed-stream and the catalyst effect. The computer program developed, using the model described above, can investigate all these effects and quantify the sensitivity of each independent parameter on the overall system efficiency, restricted, for the moment to only two important and dominating energy components. Ammonia concentration in the convertor feed, for example, is an important parameter as it determines the ammonia production, recirculation rate, and refrigeration requirement. Yuguo and Changing [59] found that, when inerts and the H_2/N_2 ratio remained constant, for ammonia content increase from 2 to 2.5%, power consumption increased from 6 to 6.1 kW-hr/kmol and ammonia production increased 3% from 985 to 1015 MTD.

Such an analysis can include compressor speed, refrigeration duty and synthesis conversion process. The compressor requirement can also be reduced by an optimization analysis to determine of the number of stages and the suction, and discharge, pressures of each stage. For a three-stage compressor, for example, the objective function to minimize the work requirement is [38]

$$f = \left[\left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} + \left(\frac{P_3}{P_2} \right)^{(\gamma-1)/\gamma} + \left(\frac{P_4}{P_3} \right)^{(\gamma-1)/\gamma} \right] \qquad (18)$$

Optimization

Optimization is a widely used engineering tool for enhancing the energy efficiency, and hence the economic competitiveness, in chemical industry. It is aimed at finding some ‘optimal’ set of design and operating parameters which enables industry to function in a ‘best possible’ way.

Design parameters, such as physical dimensions and materials of plant components, are the basis of fabrication and subsequent plant erection. Operating parameters, on the other hand, involve process variables, such as flow rates, pressures and temperatures, which are integrated into the overall plant units. As an example, a urea fertilizer chemical process plant has four large integrated units: reforming, ammonia, urea, and utilities, all of which involve inter-dependent process variables. The overall system is thus not only large in magnitude, but its interdependence in the form of re-cycle streams, for example, renders the determination of optimality as a complex non-linear problem. The process of optimization is thus both theoretical and practical as it is based on mathematical models which are non-linear and utilize material properties at actual plant conditions. These can be obtained from on-line chemical analysis during plant operation. Once formulated, the system of equations needs to be solved by analytical or numerical methods often requiring powerful computer hardware and sophisticated simulation software. Optimization analysis for a solar thermal plant requires a mathematical framework to model the underlying processes, the physical and chemical data of the plant and its materials, and numerical techniques to carry out a simulation to achieve the objective of determining optimality.

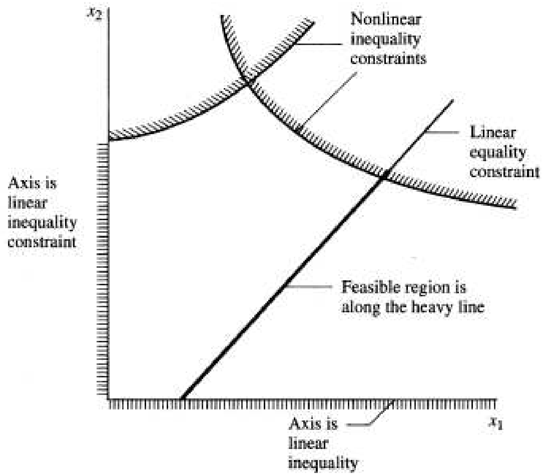


Figure 8. Optimization Process

The objective of optimization studies is to determine optimality which will result in maximum efficiency of the plant, by which it will be taken to mean optimality of the synthesis reactor in the integrated plant. Several other objectives, as diverse as plant and equipment sizing, minimizing inventory charges, and allocating resources among several processes, may be defined [26, 38]. Other terms that are analogously used for objective function, process model, and constraints are economic cost (or profitability) function and feasible solution. An optimization problem, formulated as an objective function $f(x_1, x_2)$ with two independent variables x_1, x_2, subject to an equality constraint $g(x_1, x_2) = 0$ and possibly N inequality constraints of the form $h_i(x_1, x_2) \geq 0, i = 0,1,2 \cdots N$ will then have a feasible region illustrated by Figure 8 [38]. An optimal solution will then be determined as falling in the feasible region defined as satisfying all the constraints and having an extremum. For such a problem, the dashed lines in the figure would show the infeasible regions for the inequality constraints while the solid line would show the equality constraint. Of all the values of the variables x_1, x_2 lying in the feasible region, one would need to determine the particular one set, or a number of sets, which would correspond to the extremum.

Possible obstacles in the optimization process are non-linearities, discontinuities, insensitivity of the objective function to independent variables, and local extrema confused with a global extremum.

The mathematical methodology is then identified to solve the governing equations and carry out a simulation to obtain the optimal set of parameters. These methodologies may be broadly classified as deterministic or stochastic. The former are illustrated in Figure 9 [38]. Thus, numerical techniques such as the Runge-Kutta method for solving a non-linear set of coupled first-order ordinary differential equations may be used, while the latter is based on either an analogous stochastic simulation of the phenomena or on stochastic methods to solve a deterministic set of governing equations. A typical example of a full stochastic simulation is analog, or biased, Monte Carlo simulation, while a typical example of a stochastic technique for a deterministic set of governing equations are random search methods such as Genetic Algorithms (GA).

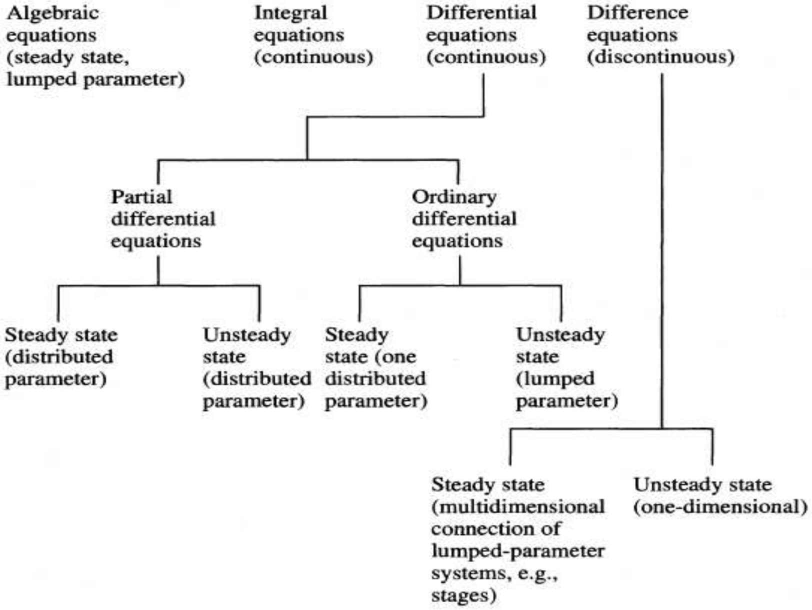


Figure 9. Mathematical Methodology to solve governing equations

One way of classifying modeling problems [38] is from the degrees of freedom $N_f = N_v - N_e$, in terms of the number of variables N_v, and the number of independent equations N_e. When $N_f = 0$ the problem is exactly determined and for a linear set of independent equations, there is a unique solution, while for non-linear equations there may be multiple solutions or no real solution. Such problems do not constitute an optimization problem. When $N_f > 0$, the problem is underdetermined and at least one process variable can be optimized, while for $N_f < 0$. Conversely, $N_f < 0$ constitutes an over-determined problem and the set of equations has no solutions and methods, such as the least squares method, can be used to determine the unknowns.

Widely used optimization methods include the following areas [38]: one-dimensional search, unconstrained multivariable optimization, linear programming, nonlinear programming, optimization involving discrete variables, and global optimization (operations research, including Monte Carlo, heuristic methods, GA and evolutionary methods). Some widely used techniques for obtaining optimality are (i) the deterministic variational functional optimality based on Pontryagin's Maximum Principle, and (ii) the Genetic Algorithm optimization search [32, 38]. The GA search method has been used [26,38] for the optimization of an ammonia synthesis reactor [38] shown in Figure 10.

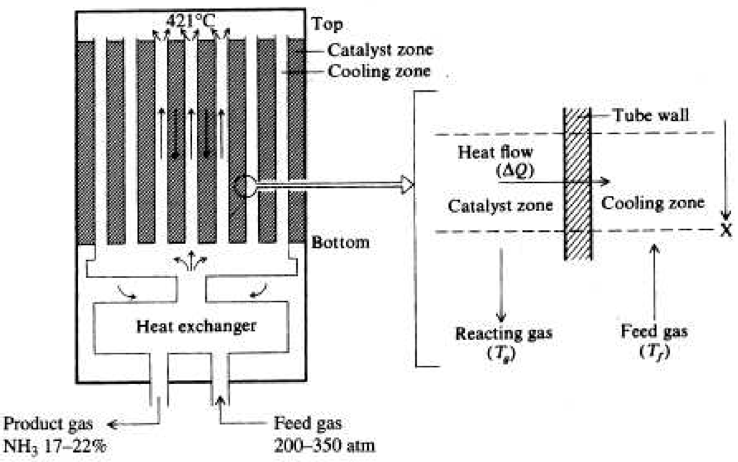


Figure 10. Ammonia Synthesis Reactor

First, the governing equations are numerically solved to obtain the temperature and concentration profiles shown in Figure 11.

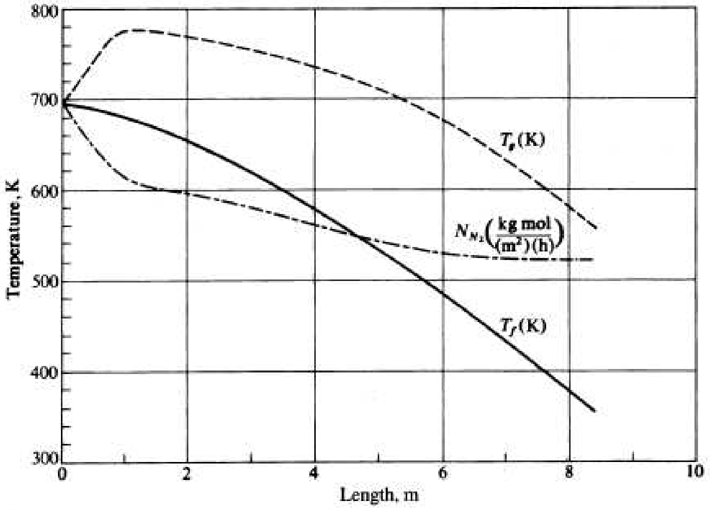


Figure 11. Temperature & Concentration Profiles along Converter Length

The numerical solution is followed by an optimization exercise in which an objective function $f(x, N_{N_2}, T_f, T_g)$ is defined along with the three governing equations, taken as constraints. Thus, the problem has one variable (*x*; the reactor length) one degree of freedom $(N_f = 1)$ and, being underdetermined, can be solved for optimality. The GA search is carried out as shown in Figure 12.

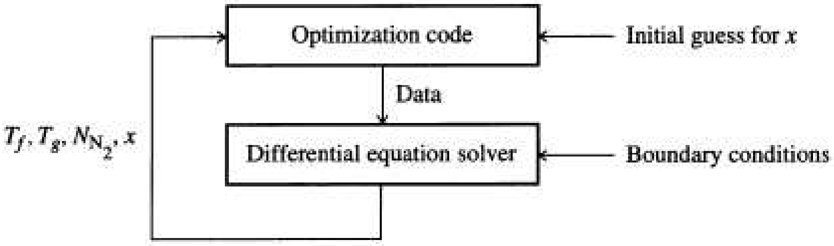
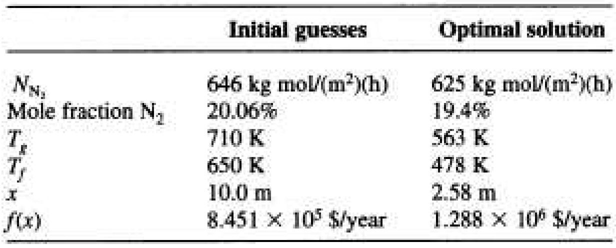


Figure 12. GA Search Algorithm

The optimal solution found for the exit conditions shown in Table 2.

Table 2. Optimal solution for the exit conditions



	Initial guesses	Optimal solution
N_{N_2}	646 kg mol/(m^2)(h)	625 kg mol/(m^2)(h)
Mole fraction N_2	20.06%	19.4%
T_g	710 K	563 K
T_f	650 K	478 K
x	10.0 m	2.58 m
$f(x)$	8.451×10^5 \$/year	1.288×10^6 \$/year

The optimization thus concludes that a 10*m* reactor results in an optimal solution for the values given above

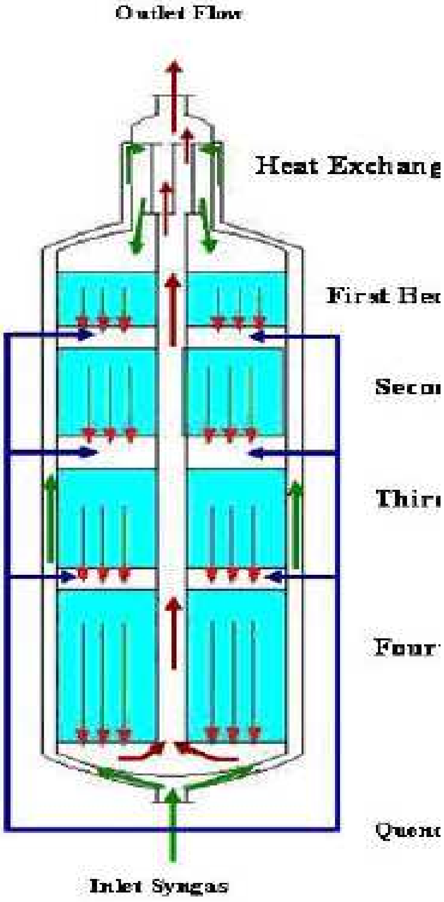


Figure 13. Four-Bed Synthesis Reactor

Sadeghi and Kavianiboroujeni [21] have used the Genetic Algorithm for a 1-D and 2-D optimization of a Kellog-type ammonia plant, located at Khorasan (Iran). The axial reactor (Figure 13) has four promoted-Fe catalytic fixed beds with a heat exchanger at the top. Syngas flows vertically upwards in the spaces between the two walls of the reactor, where it is pre-heated, then turns down through the beds and from the bottom fourth bed again turns upwards, exiting from the top of the reactor. The independent parameters investigated are the quench flow and quench temperature. Between the beds, the hot syngas is mixed with quench streams (shown in three streams between the beds) to control the temperature.

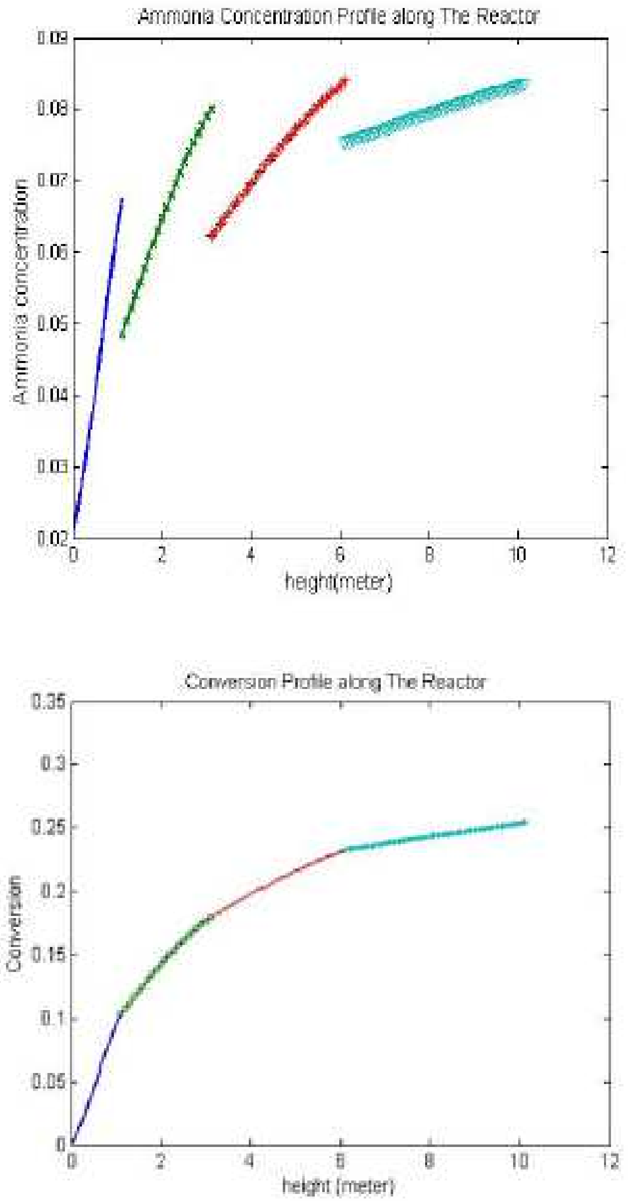


Figure 14. Effect of Quench gas on conversion efficiency

The purpose of injecting the quench streams is, clearly, to increase the ammonia production from the reactor; and since the forward synthesis chemical reaction is favoured by high pressure and low temperature, the challenge is to reduce the temperature at every bed exit. The ammonia and nitrogen conversion obtained by Sadeghi and Kavianiboroujeni [21] by a numerical solution of the mass and energy balance equations is shown in the Figure 14. It can be seen that most of the ammonia conversion takes place in the first bed even though it is the shortest. The effect of the quench gas is to reduce the ammonia conversion after every bed exit but this picks up as flow proceeds.

The paper uses GA for obtaining optimal temperature distribution, in this nonlinear optimization problem, resulting from a given quench flow, and subsequently optimal quench flow given quench temperature. In the optimization problem, the objective function is the ammonia outlet flow-rate, while the constraints are (i) $T < 800K$, in the reactor for avoiding hotspots, (ii) an ascending nitrogen conversion during optimal flow: $Z|_x < Z|_{x+\Delta x}$, and (iii) for the syngas: $T_{in} < T_{out}$.

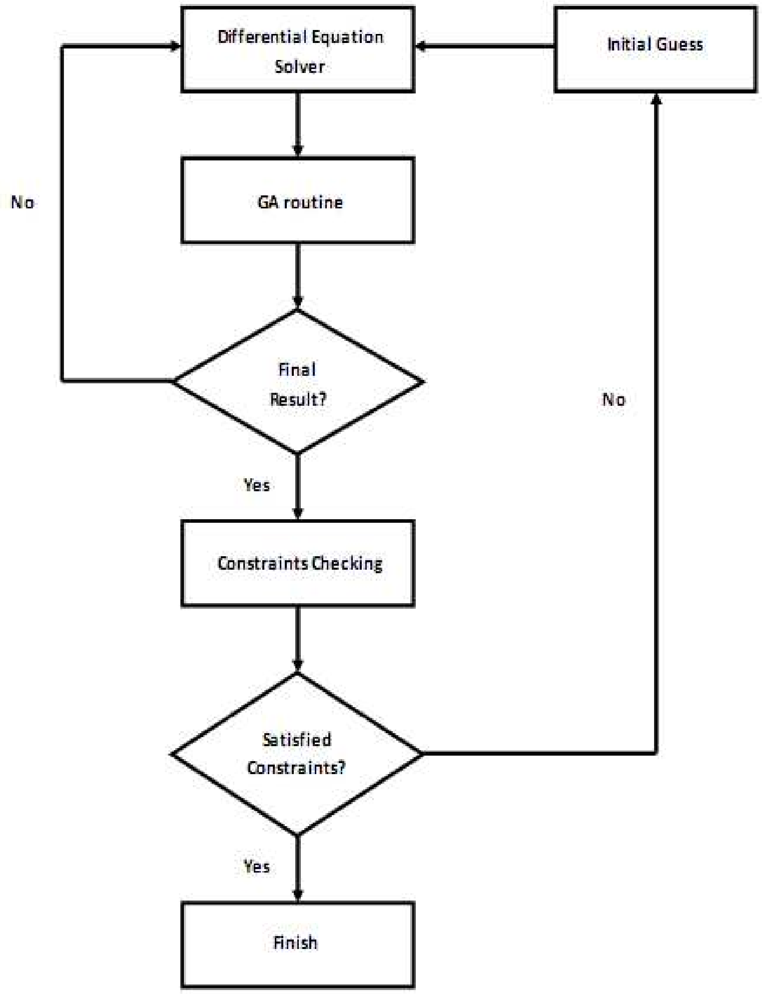


Figure 15. GA Algorithm for obtaining optimal temperature distribution

The flow-chart, Figure 15, for this optimization is reproduced from the paper [21] and their results, in Figure 16, give maximum ammonia conversion at a quench temperature of 650 K and a maximum conversion flow-rate of 47%

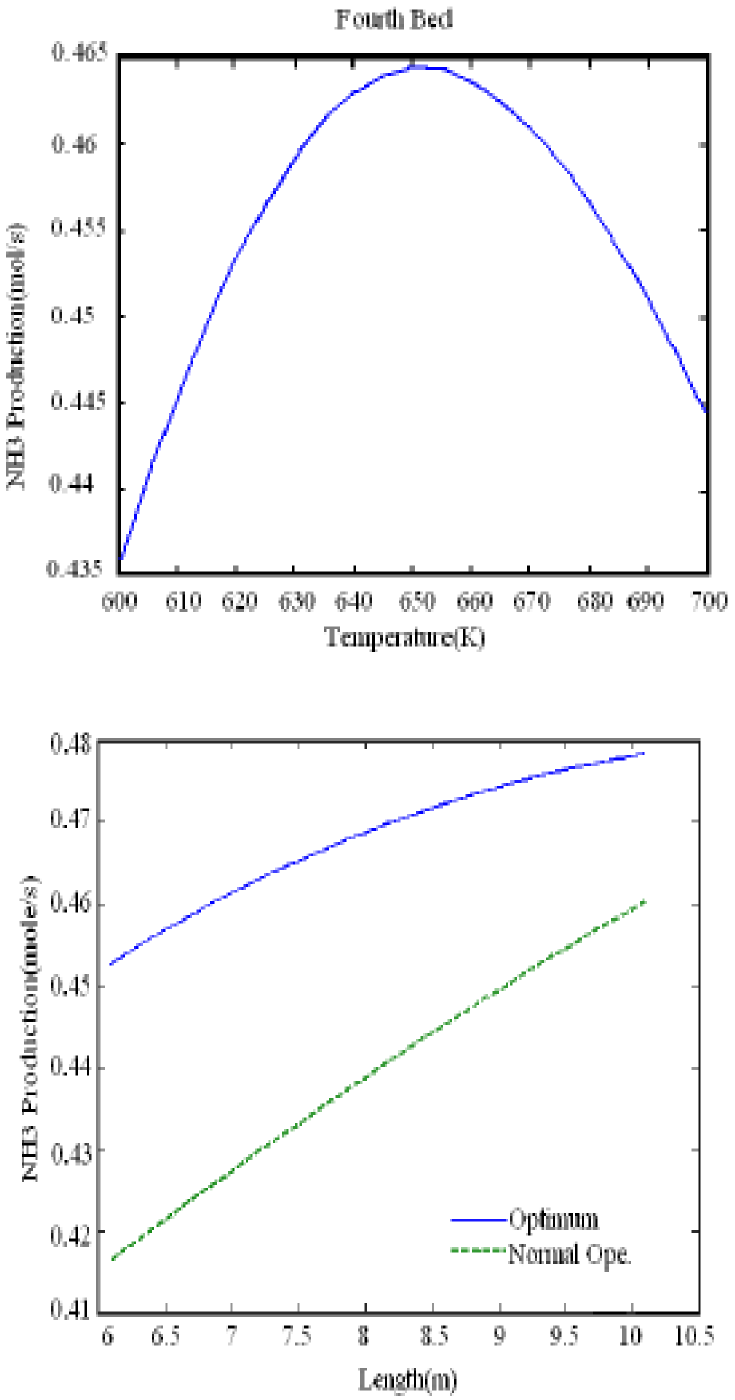


Figure 16. Optimal and Normal Ammonia Production rates

The important changes between normal and optimal operations for nitrogen conversion and reaction rate are shown in Figure 17.

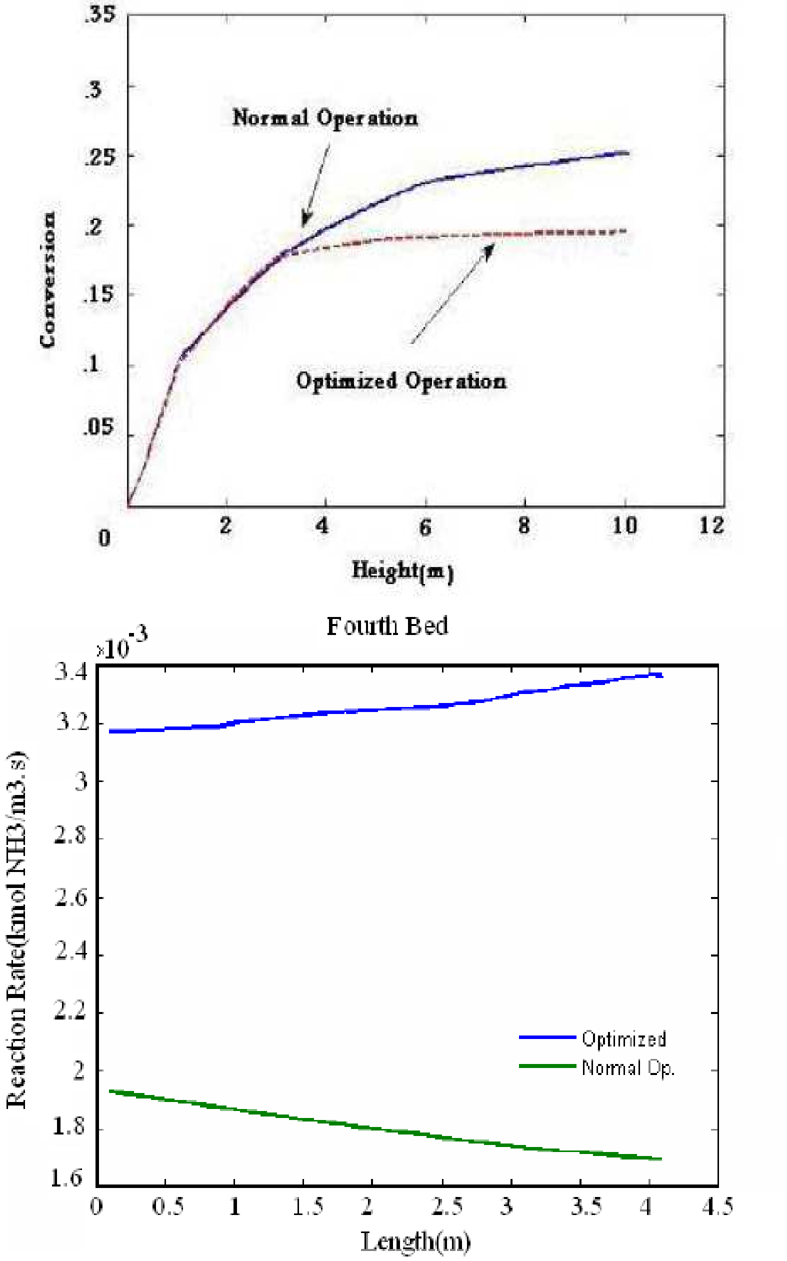


Figure 17. Optimal and Normal Nitrogen Conversion and Reaction rates

GA used for obtaining optimal temperature distribution has increased the ammonia production of the Khorasan plant by 3.3% (8,470 tons per year).

When the reactor is isothermal, different catalysts can be loaded to enhance productivity and when it is non-isothermal i.e. it has temperature gradients, then the catalyst may be non-uniformly loaded or different catalysts may be used for different temperature regions, to enhance productivity. Finding the optimal (spatial) distribution of catalyst is crucial to optimizing the performance. Numerical search can be carried out by dividing the reactor in zones and assuming uniform values of catalyst material in each zone; this will mostly result in a sub-optimal solution.

Variational methods have also been used to find optimal configurations for process variables in a synthesis convertor. These methods originate from the works of Leibniz (1646-1716) and Newton (1643-1727) credited for inventing and formalizing Calculus; followed by "Variational Calculus" attributed to Leonhard Euler (1707-1783) through his published work of 1733. Among the several contributors to variational calculus were Lagrange (1736-1813), Legendre (1752-1833), Gauss (1777-1855), Cauchy (1789-1857), and Poisson (1781-1840).

The field of Optimal Control [68] is an area of optimization in which the "best possible" strategy is chosen using the calculus of variations. While calculus can be used for optimization of a function of variables, calculus of variations is used to obtain the extremum, or stationary condition, of a functional (function of a function) by finding the function which extremizes the functional. The first variational calculus optimal problem was the Brachistochrone (shortest time) Problem solved by Bernoulli in 1696 [71] The formulations used are by Lev Semenovich Pontryagin (1908-1988), who developed the Maximum Principle, and the terminology of "Bang-Bang control" to steer a system with maximum or minimum control parameters, and of Bellman (1920-1984) who extended works of Hamilton (1805-1865) and Jacobi (1804-1851) to the now well-known Hamilton-Jacobi-Bellman (HJB) equations in Dynamic Programming.

Variational calculus [69, 70, 71] is used in areas that include optimal control, particle transport, mechanics, optics and chemical plant design [see *e.g.* 63]. There is a vast range of problems that determine complexity, such as whether the functional involves one or several functions, derivatives of functions, and one or more than one independent variable. Another class of variational calculus problems involves constrained problems with algebraic, integral or differential equation constraints.

Industrial Applications of Modeling and Simulation

The purpose of simulation is to estimate the best possible synthesis conversion, by optimizing the catalyst distribution, to investigate the feasibility of such base-load operation. A TSP will have operational parameters, pressures, temperatures and flow rates, similar to those in the ammonia units of urea fertilizer plants in the chemical process industry. These require pressures in the range of 130-250 bar and temperatures in the range 250-600 ^{o}C. Such high pressures require compression which is expensive in terms of equipment cost as well as energy utilization.

The conventional sequence of process steps are optimized by the introduction of improved catalysts (KM high strength, versatile, stable and poison-resistant catalyst, mainly magnetite Fe_3O_4 with promoters mainly oxides of calcium, aluminum and potassium, operating temperatures 340-550 ^{o}C [7]), new equipment design (such as improved synthesis converters), and process optimization studies. The carbon monoxide concentrations have been minimized at the exit of the shift converters, and a low-energy carbon dioxide removal process (such as selexol) has been used. New syn converters S-250 and S-300 are improved versions of the previous single bed S-50 and two-bed S-200 radial flow converters. Topsoe recommends S-300, developed in 1999, for all new plants [5].

Ammonia converter features, listed in Table 3, are taken from Topsøe [13], and depict the technology improvements over thirty years.

Table 3. Converter features

Type	Basic Design	Comments
S-50	One catalyst bed	Simplest and cheapest
S-200	Two catalyst beds and one interbed heat exchanger	Commissioned in 1979; 130 units installed
S-250	Combination of the S-200 followed by the S-50	
S-300	Three catalyst beds with two interbed heat exchangers	Higher conversion for same catalyst volume of S-250; installed first in 1991.

Modeling can also be used to investigate the effect of system pressure, catalyst activity and catalyst bed physical dimensions in KBR plants using a high-activity graphite supported ruthenium catalyst, typically three stages, after one stage of traditional iron catalyst. This is claimed to increase the activity 10 to 20 times [6] enabling very high conversion at a lower pressure of 90 bar.

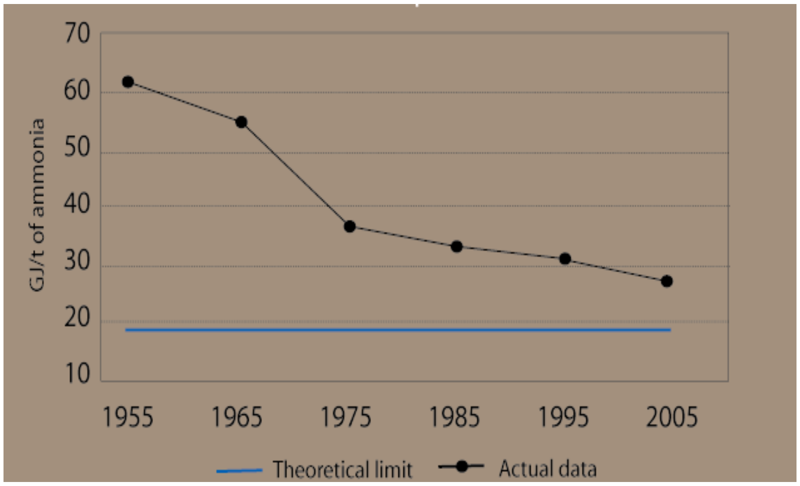


Figure 18. Energy Consumption Trends in the World- Ammonia Plants

A typical 1500 TPD ammonia plant [23], uses 257 TPD hydrogen and 1237 TPD nitrogen. The natural gas feedstock is 36,000 SCFH (2,760 lb-mol/hr), 86,000 SCFH (4,800 lb-mol/hr) air, and 150,000 PPH (8,280 lb-mol/hr) of steam. Modeling can be used to minimize the compression and refrigeration requirements and maximize the synthesis heat recovery.

This plant has an ammonia reactor catalyst bed size 3230 ft^3, and the total catalyst requirements are approximately 15,000 ft^3 (including reformers, HTS, LTS, methanator, de-sulpherizer). The total material cost of catalyst is approximately US$ 8 million (assuming catalyst is acquired once per year). At a natural gas price of US$ 7.06 per MMBtu, the gas price is US$ 40 million per year. These two material costs account for about 98% of the total material cost, the remainder being the plant water for steam production.

Such a plant results in a production cost of US$ 195/tonne compared with the purchase cost of ammonia of US$ 330/tonne. Accounting for electric and indirect costs, the profit of such a plant is in the range of US$ 60-70 million per year depending on the number of days for plant turnaround in a year. The energy consumption quoted in the report is 5.3 MMBtu/tonne Ammonia = 5.6 GJ/MeT (1Btu = 1055 J). This is a useful figure-of-merit, and as shown in Figure 18, has improved by a factor of two over the last fifty years.

Optimal control methods have also been used to obtain the optimal temperature and concentration profiles in ammonia synthesis reactors [61, 62].

Process simulation, based on the laws of conservation of mass, momentum and energy, together with equations of state and thermo-physical or chemical kinetics data, can be used to carry out steady-state as well as dynamic simulation, depending on whether the focus is on solving for process variables in stationary or time-dependent environments. The aim, of course, is to optimize design and operations so that systems perform with maximal efficiencies translating into maximizing organizational profitability.

Dynamic simulation can be used for a wide range of operational and trouble-shooting issues in chemical industry, such as on-line simulation to control a plant or for training plant operator, and for off-line dynamic simulation is used for process optimization, or to study a process change

In the 1960s, process simulation consisted of solving conservation equations by extensive number-crunching with computer programs written in FORTRAN on large main-frame computers such as VAX, IBM and CDC. Many of these were converted into C++ for object-oriented software environments. This was followed by user-friendly GUI software carrying out essentially the same computations but in an easy-to-use manner.

The current trend in industry is to use commercial process simulation suites or custom designed process simulators to simulate the large, complex and inter-connected industrial processes that represent an actual chemical plant. This ranges from small batch plants to large process fertilizer and petrochemical industry. The commercial suites currently in extensive use include ASPEN HYSYS, CHEMCAD, HYSIM, and WINSIM. ASPEN Plus includes Basic engineering (simulation to PFD, PFD to P&ID).

Conclusions

Mathematical modeling and simulation has been used for the design of ammonia plants and to optimize their performance. The models are based on the laws of conservation of mass, momentum and energy for multi-species mixtures. The chemical reactions are modeled by appropriate thermodynamics and kinetic rate laws. The resulting equations are thus non-linear, coupled, partial differential equations which require numerical computing methods to solve for the process variables.

This paper reviews the mathematical models and the simulation that has been carried out for ammonia synthesis. Optimization methods, both deterministic and stochastic, are also reviewed. These, as well as variational optimal control methods, have been aimed at maximizing the ammonia conversion, and hence the overall efficiency of a thermal storage plant, by estimating optimal process variables.

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