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Solar Thermal Energy Storage using Liquid Ammonia Systems in Industry

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Abstract

The success of solar thermal systems for electricity production hinges very crucially on the selection, mechanical design and optimal operation of an energy storage system which can enable the continuous operation of a power plant. The energy storage systems being investigated include solid graphite, encapsulated Phase Change Materials (PCMs) and liquids such as water and ammonia. A storage option being investigated for large solar-thermal systems is liquid ammonia which by its endothermic dissociation converts to nitrogen and hydrogen gases, and can be synthesized exothermically to recover heat when required. Ammonia is an abundantly produced chemical, globally and in Pakistan. The synthesis of ammonia with carbon dioxide results in the formation of urea fertilizer, or carbamide $(NH_2)_2CO$ at pressures and temperatures of the order of 150atm and 600K respectively. In Pakistan there are eight large urea fertilizer plants based on the reforming and synthesis of natural gas mainly from the Sui and Marri gas fields. This work considers the potential of liquid ammonia as a storage medium especially with regards to its integration into a urea fertilizer Chemical Process Industry (CPI) infrastructure. We discuss essential thermodynamic and reaction kinetic features underlying the process and then focus on the energy balance of a solar thermal plant which requires compressed syngas for an ammonia reactor. A mathematical model, based on the material and energy conservation of constituent gases is used to obtain information on the process dynamics in a synthesis convertor. From this, the energy production from synthesis is estimated and compared with the compression energy requirement. We are able to demonstrate that compression power is a major concern for future thermal storage systems and may well be the single determining factor in the viability of such renewable energy systems.

Introduction

The continuous electricity generation by solar thermal systems hinges so crucially on the storage mechanism that success in this area may well determine its future. This work considers one such mechanism – the use of liquid ammonia through its dissociation and synthesis reactions – for electricity generation in the absence of solar flux. The objective is thus to consider the feasibility of, the process itself, its integration into an existing Chemical Process Industry (CPI), such as urea fertilizer, and to estimate the process efficiency.

The first issue requires consideration of the chemical process and the operating parameters including pressure, temperature, and reaction kinetics etc., in the context of solar thermal energy obtainable from a solar dish receiver facility. For the possibility of integrating such a Thermal Storage Plant (TSP), we consider the operating parameters in a candidate CPI taken to be representative of the urea plants operating in Pakistan. As of 2010, there are eight urea producing CPIs in Pakistan [3] with a total production in 2008-09 of 4.918 million tonnes. At an international price of US$ 300/tonne, this represents an annual sales value of US$1,500 million. This amounts to an average production of about 1600 tonnes per day (TPD) per plant.

We consider a simplified TSP model [4] shown in Fig. 1, as this includes the essential features to estimate the power requirements associated with the process flow diagram. The input syn gas stream (ST1) will be available to the TSP from the day-cycle operation of the solar plant. This feed-stream will be compressed to the temperature and higher pressure required for synthesis, typically, of the order of 266°C and 135 bar. The 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 and produces 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.

The work of this paper focuses on the energy balance of the considered process flow diagram (PFD). The 'energy input' components are thus the compressors (C-1, 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. In order to estimate all these quantities, and hence the overall efficiency of this plant, we will require a model to compute the process variables for all streams in the PFD.

The model will be based on material, momentum and energy conservation equations for the components, and power requirements for the compressors. We can also determine the compression requirement for recycle in the convertor, refrigeration duty, vaporizer and purge systems but here restrict the analysis to syngas compression and exothermic energy availability.

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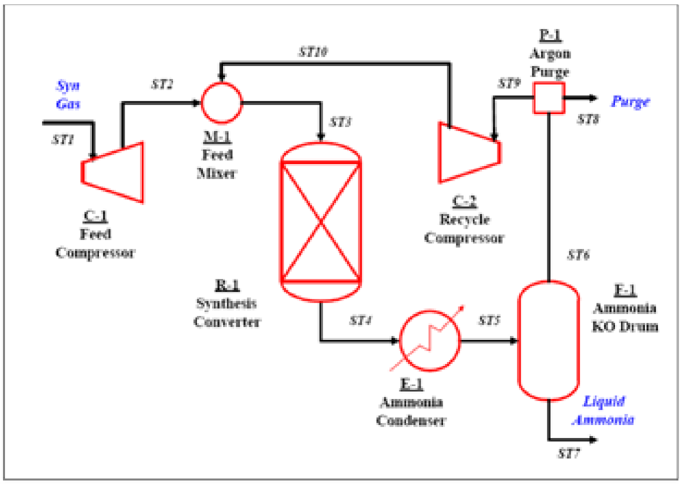

Figure 1: Ammonia synthesis energy recovery system for a Thermal Storage Plant.

In the present analysis, we consider a ‘stand-alone’ TSP as it is understood that a Rankine-cycle solar plant [2] produces the syn gases from the dissociation of liquid ammonia during the day-cycle operation. While the primary objective of this paper is the estimation of the efficiency from the overall energy balance, an important objective will also be to determine the compression requirements for the storage of syn gases from the day-cycle operation to lessen the load on the TSP and subsequently to increase its attractiveness. 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 NH3 synthesis exothermic reaction.

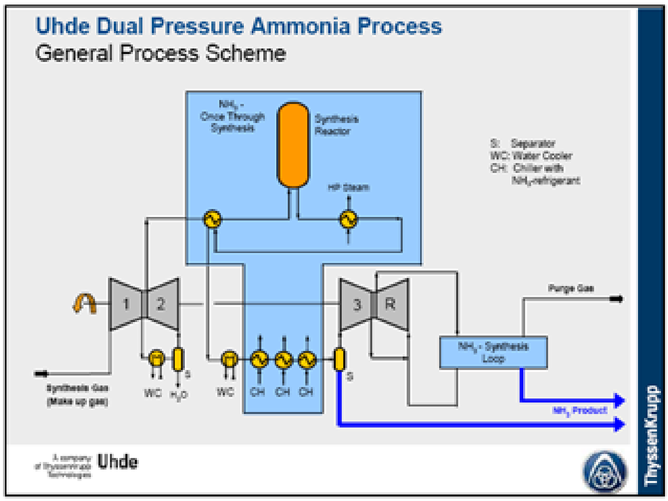

Figure 2: An optimized ammonia synthesis process by Uhde.

An “optimal configuration”, such as the Uhde Dual Pressure Ammonia Process, shown in Fig. 2, including optimization of compressor power, pipes and valves for high-pressure operation may hold the answer to the viability of ammonia as a thermal storage medium.

The Model

The model is based on thermodynamics, fluid-flow and reaction kinetics of the processes in the TSP considered. For a compressor, we can estimate the power requirements [5, 6] for isentropic compression, as

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

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

(2)

More generally, for a multi-stage compressor with *n* units [5], with the compression ratios (*r*) in all the stages equal, the total work can be estimated from

$$W_s = \frac{n\gamma}{\gamma - 1} R\,T_1 \left[1 - (r)^{(\gamma-1)/\gamma} \right] \qquad (3)$$

where, for an ideal gas $PV = R\,T_1$ The above expressions are based on the assumption that specific heats remain constant in the pressure and temperature range. In this analysis, we obtain compression power requirements for a single-stage reciprocating compressor, and discuss the possibility of optimization in the use of multistage compression with optimal interstage pressure ratios.

For the synthesis process, we begin with the conservation equations for chemically reacting species [7] and used by Dashti [9]. These are also used for an overall plant balance by Yuguo [8] and for an optimal analysis by Nummedal [10].

$$\frac{dz}{dx} = \frac{\eta R_A}{2F_N^o / A} \qquad (4)$$

$$puC_P \frac{dT}{dx} + (-\Delta H_r)\eta R_A = 0 \qquad (5)$$

In the above, represents the fractional conversion of nitrogen, x is the distance from the top of the catalyst bed, is the initial molar flow rate of nitrogen, ρ is the density, and is the heat of reaction.

All the expressions for specific heat capacity, heat of reaction, and activities have been taken from Dashti [9], Narayanan [8] and verified with the NIST [12] database.
For the reaction kinetics, we use the Temkin-Pyzhev [8,9] form of the synthesis reaction rate as a function of the pressure, temperature, and activities

$$R_A = 2k\left[K_a^2 a_N \frac{a_H^{1.5}}{a_A} - \frac{a_A}{a_H^{1.5}}\right] \qquad (6)$$

where the activities are defined as in terms of the molar fractions and the fugacity coefficients . The equilibrium constant is given by

$$\log \qquad 2.691122 \log \qquad 5.51925 \quad 10$$

$$1.848863 X 10^{-7} T^2 + \frac{2001.6}{T} + 2.689 \qquad (7)$$

and the reaction constant is given by the Arrhenius rate form as

$$k = k_o \exp\left(-\frac{E}{RT}\right) \qquad (8)$$

where E is the activation energy.

This is demonstrated by considering Fig. 3 and Fig. 4 in conjunction, where the equilibrium constant shows a decline in response to increased ammonia output as the process temperature rises. It clearly shows that the process is feasible at temperatures exceeding 550K and increases as the temperature increases.

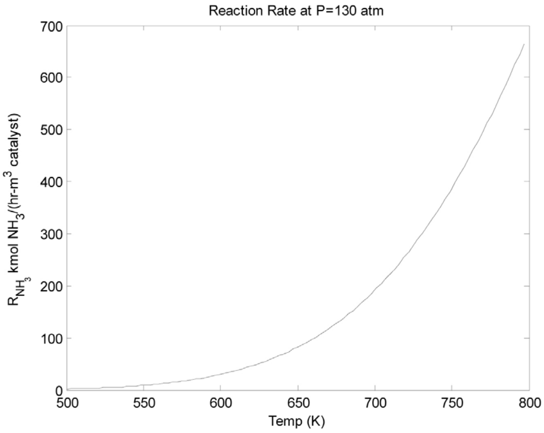

Figure 3: Reaction rate of ammonia synthesis for an initial composition (mole fractions) of H2= 0.6567006; N2= 0.2363680; Ar= 0.0202874; NH3= 0.026930; CH4= 0.059714.

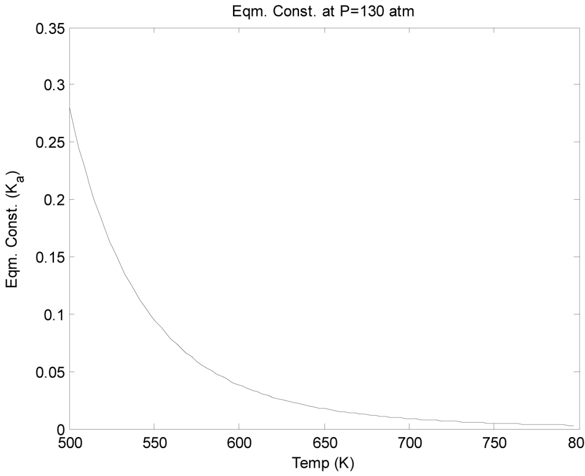

Figure 4: Equilibrium constant for ammonia synthesis.

The overall synthesis rate (kmol of ammonia prduced per hr per unit volume of catalyst) is where is the catalyst effect factor [9] and may have a significant effect on the overall efficiency. Figure 5 shows as a function of the catalyst temperature at 150 atm, for three values of the conversion of nitrogen as the syngas flows along the catalyst. It indicates that temperature outside a certain range (570-650K) may significantly retard the conversion process and subsequently reduce the overall plant efficiency.

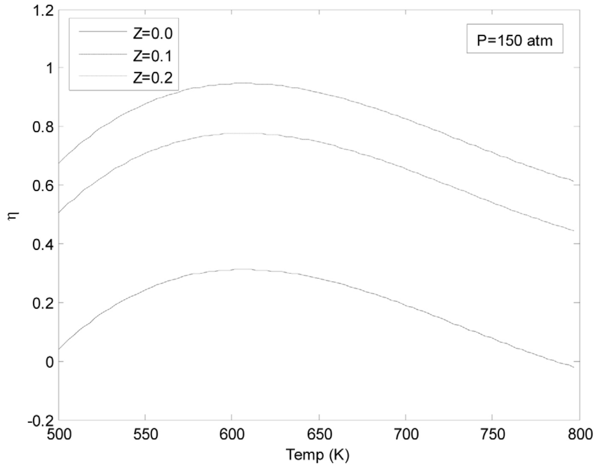

Figure 5: Effect of convertor temperature on catalyst

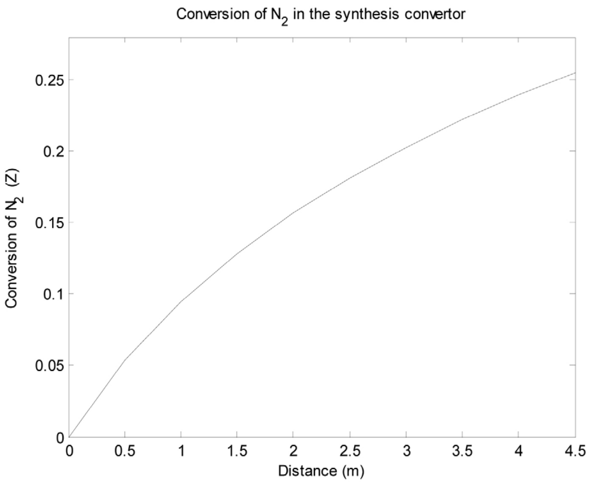

Figure 6: Conversion of Nitrogen along a single-bed catalyst

Figure 5 shows that the effectiveness of the catalyst increases significantly as nitrogen conversion to ammonia takes place but decreases with an increase in temperature. This is an important observation as it shows that the upper part of the catalyst is less effective than the middle and lower parts where more conversion has taken place. However, as conversion increases, the temperature of the catalyst bed also increases and subsequently the effectiveness decreases. Thus it is good industrial practice to remove heat by an inter-bed heat exchanger and to introduce some recycle syngas.

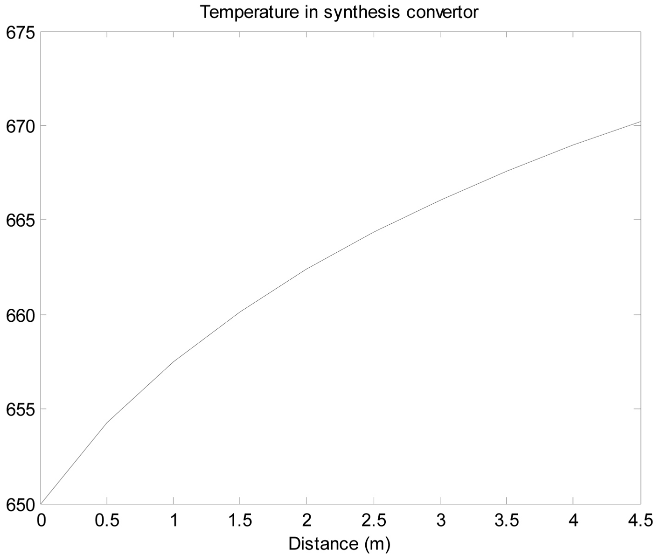

Figure 7: Syngas temperature in convertor.

Results

The simulation process for results presented in this paper use the compressor and synthesis convertor model described above. We specify process variables for input stream ST1, as shown in Fig. 1. From these, and the requirements of stream ST3, the compression power is estimated. Subsequently, the material and energy balance equations are numerically solved to obtain the molar flow rates and temperature of the syngas in a single-bed catalyst convertor. For a plant of magnitude similar to that described in Dashti [9], which has 183600 kg/hr of input flow rate to reactor and the mole fractions shown in Fig. 3., we obtain results for the nitrogen conversion, syngas temperature and molar flow rates shown in Figs. 6-8.

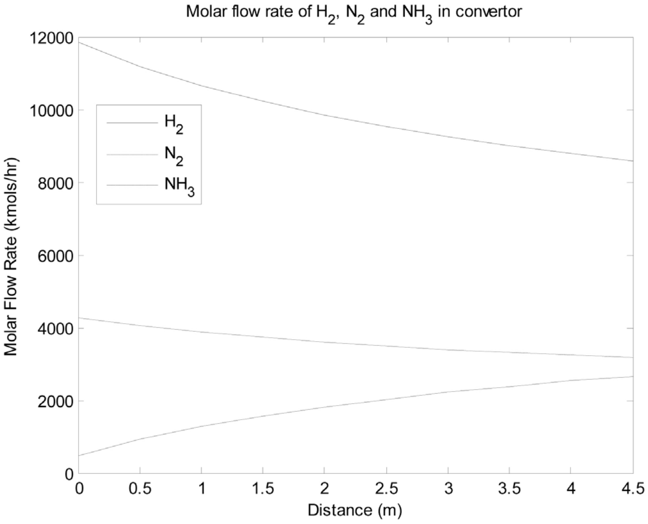

Figure 8: Molar flow rate in convertor.

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 must be assessed in comparison with the syngas compression requirement shown in Fig. 9. As shown, the compressor power is dependent on the syngas flowrate, 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).

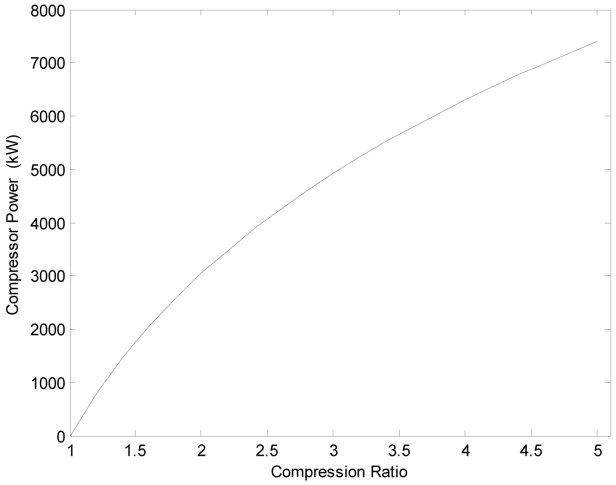

Figure 9: Syngas compression requirement as a function of compression ratio.

Conclusion

This work estimates the two dominating energy factors of a thermal storage plant based on the This work estimates the two dominating energy factors of a thermal storage plant based on the endothermic dissociation and exothermic synthesis of ammonia. It was determined that the syngas compression may greatly exceed the useful work realizable from such a plant. In this study, the compression ratio required for the syngas was sufficient for a single-stage reciprocating compressor and even for such a favorable input, the power requirement was as large as 5 MWe. In case a TSP is isolated from industry and storage of syngas is not available at such high pressures, the compression power requirement can be even greater. For the case considered here, the exothermic thermal power is 32.4 MW(th) which at a conversion efficiency of about 30% would be about 10 MWe. When recycle compression is considered, the efficiency of the plant may further deteriorate. Factors to investigate in greater detail include the hydrogen/nitrogen ratio, the purge gas ratio, the ammonia content of the convertor feedstream and the catalyst effect.

Future work will 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 [11] is

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

The computer program developed, using the model described above, permits us to 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 Changying [8] found that, when inerts and the H2/N2 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 tonnes/day.

This paper concludes that compressor duty is comparable with the power output from a TSP based on liquid ammonia for storage.

Acknowledgement

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