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Ammonia Plant Analysis

Piyush I. Modi, Prof. C.G. Bhagchandani
L.D. College of Engineering, Ahmedabad
modi_00973@yahoo.co.in, cgbhagchandani@rediffmail.com

Abstract

The efficient operation of existing plants in the process industry requires their analysis through simulation together with power and heat integration by retrofitting. Pinch Analysis (PA) is a classical procedure to achieve this goal. Yet, a further integration can be obtained reducing the entropy generated in the chemical processes.

Ammonia, important as raw material in many process industries, represents the primary feedstock for the nitrogenous fertilizer industry, being produced from its elements through a very exothermic reaction.

The ammonia synthesis process is characterized by high reaction temperatures and pressures, thus needing high power requirements. It represents a typical reaction-separation system with a recycle stream ("ammonia synthesis loop") and a cold separation train for the main product. The recycle is the consequence of the thermodynamic equilibrium limitations, implying low degrees of hydrogen-nitrogen mixture conversion to ammonia. The chemical driving force is improved removing the ammonia at low temperatures and recycling the unreacted species back to the reactor.

Thought in cascade with pinch analysis, the chemical reactors energy integration (CREI) concept focuses on, simultaneously, the entropy generation reduction of both chemical reactor network (CRN) and heat exchanger networks (HEN). It replaces the chemical reactors with virtual heat exchangers generating the same amount of entropy. CREI analysis aims to improve the reaction heat utilization and to reduce the operating costs. The energy savings lead to an important emission reduction, in the ammonia plant (less fuel has to be burnt), in the energy production sector, since less energy is needed for compression and refrigeration and, also, in the utilities generation area.

The ammonia synthesis loop was modelled using Aspen Plus® as process simulation software. Cascaded Pinch and CREI analysis of the process generated a suitable network configuration and operating parameters that minimize the entropy generation.

Key words – Ammonia synthesis loop, simulation, operating parameters

1. Introduction

Due to its massive use in agriculture, where it is essential in meeting the food production for the growing population, ammonia became one of the largest bulk chemicals in the world. It is produced in large amounts despite the specific energy consumption (SEC) of 35–50 GJ per ton of ammonia, depending on the raw material and the process, which makes it one of the highest energy-consuming product. In the ammonia plants, natural gas, naphtha or LPG is the common feedstock. Reduction of the SEC not only saves fossil fuels, but also diminishes the carbon dioxide emission. The technology used in ammonia plants is mature, so further reduction of SEC can mainly be expected due to better process integration. The trend is to consider both the heat exchanger network (HEN) and the chemical reactor network in the combined heat and energy integration.

The main environmental problems of the process are the direct emissions from the combustion of the raw material and the indirect ones, due to the consumption of cooling water and electrical energy for the two compressors and the refrigeration cycle. The environmental impact of the latter, measured CO_2, SO_x and NO_x emissions, results from the combustion processes in the power plants.

Ammonia synthesis from hydrogen and nitrogen is restricted by the unfavourable position of the chemical equilibrium and by the relatively low activity of the promoted iron catalyst. The equilibrium concentrations of species in the ammonia synthesis reaction depend mainly on the pressure and the temperature, the concentration of inerts being less important. As catalysts are active over the narrow temperature range of 380–500 ^{0}C and unable to approach more than 80% of the equilibrium, the maximum ammonia concentration in the recycling gas at the reactor outlet depends in fact only on the pressure. Even at high pressures up to 30 MPa, less than 26% of the synthesis gas is converted to ammonia per pass. The unreacted hydrogen-nitrogen mixture is returned to the reactor after the removal of product by its condensation at low temperatures. The energy consumption for ammonia production depends strongly on the ammonia loop design.

The synthesis loops are generally of two types. The first type recovers ammonia product after make-up gas-recycle compression. In this case the synthesis gas is purified by the washing action that the condensing ammonia has on the make-up gas; the drawback is that it requires slightly larger compressor power because the converter effluent undergoes recycle compression before product condensation. Most modern

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designs, developed to reduce the energy consumption in the ammonia plant, employ molecular sieves as driers at the interstage of the synthesis gas compressor to purify the make-up gas, allowing the synthesis gas to be fed directly to the converter. Thus, the converter effluent is not saturated by the make-up gas addition, allowing some product recovery to be shifted to cooling water. This also lowers the ammonia concentration in the converter feed, resulting in a greater driving force for the ammonia synthesis reaction. In both arrangements the synthesis gas delivered to the ammonia converter is extremely pure because of the washing action the condensing ammonia has on the incoming make-up gas ridding it of impurities. The result is an extremely long catalyst life, even up to 20 years.

Industrial ammonia synthesis presents one of the most attractive opportunities of application of second-law based thermal and energetic integration methods in process engineering. Energy analysis is based on the second law, and generally allows the causes and locations of process inefficiencies to be better pinpointed than does energy analysis, and efficiencies to be more rationally evaluated. Energy is consumed during real processes and conserved during ideal processes. The energy consumption during a process is proportional to the entropy created due to the process irreversibilities, so the results obtained using either criterion should be equivalent. The employment of process energy-integration technology is an important approach for reducing energy consumption in the chemical process industry and PA has been proved to be efficient in developing the best integrated process designs for both new plants and retrofits. But, PA addresses only the HEN, so new approaches should be developed to consider the other major source of entropy generation, the CRN. The concept of chemical reactors energy integration (CREI) deals with this problem, minimizing the global entropy generation while keeping the state and working parameters of the reactor in the range of industrial interest. The main ideas of CREI are: A) the replacement of the chemical reactor with a system of two or three virtual heaters/coolers (defined as one-stream devices), encompassing a heat exchanger structure which destroys the same amount of energy as the original chemical reactor and B) the theoretical reversible temperature. It should be pointed out that CREI analysis is a hybrid method, tempting not only the local reduction of the generated entropy for each chemical reactor, but also the flowsheet generated entropy diminution, even allowing some increase in the local chemical reactor's entropy production if this is in agreement with the abovementioned global goal.

2. The ammonia plant analysis

Commercially available flowsheet software AspenPlus® 11.1 of Aspen Technology, Inc. was used as simulator to develop the process model. Flowsheet programs are mathematical tools for steady-state and dynamic simulation of complex chemical plants. Their main advantage lays in their data banks for the computation of the species physical properties. Using flowsheet software, the developing time of ammonia synthesis process model can be reduced drastically and, furthermore, process evaluations like case studies, sensitivity analysis or optimization become possible. The thermodynamic property model used for the flowsheet presented in Figure 1 is UNIQUAC with Ideal gas and Henry's laws.

The distinctive feature of the ammonia plant is the presence of a network of six chemical reactors, in five of them the corresponding chemical process being exothermic. It is worth mentioning that, although in the secondary reformer the process is slightly exothermic, the rector is heated in order for the chemical process to take place with a convenient reaction rate. The entropy generated at the plant level is 788.3 kW/K.

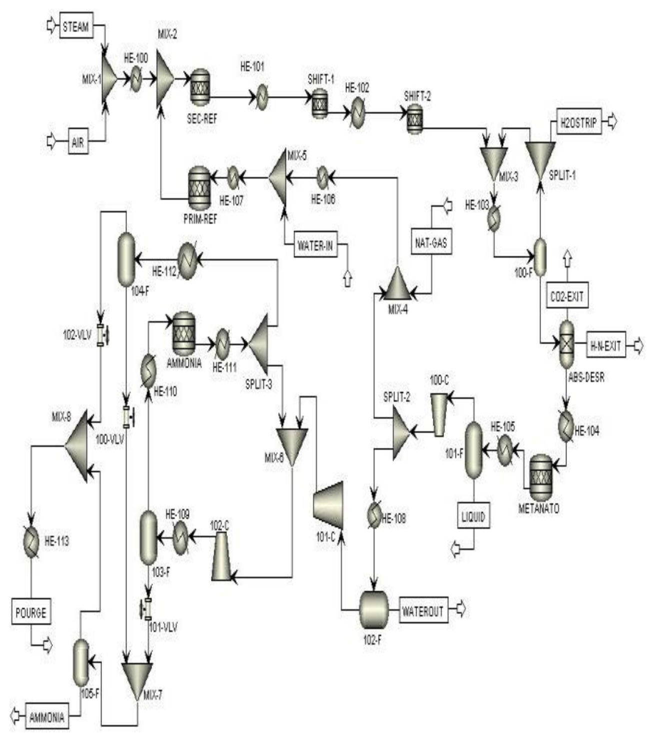

Figure 1. Flowsheet of the ammonia synthesis.

The ammonia plant was first analyzed using the pinch methodology, as implemented in the Super Target's Process® of Linhhoff March, Ltd. The Balance Composite Curves resulted from PA is presented in Figure 2. The new flowsheet (not presented due to the lack of space) has a modified HEN of 44 units, which represents a rather high increase compared to the base case, but the generated entropy at the plant level dropped to 338.9 kW/K, , 57 % less than for the base case , which represents the maximum possible reduction with this technique.

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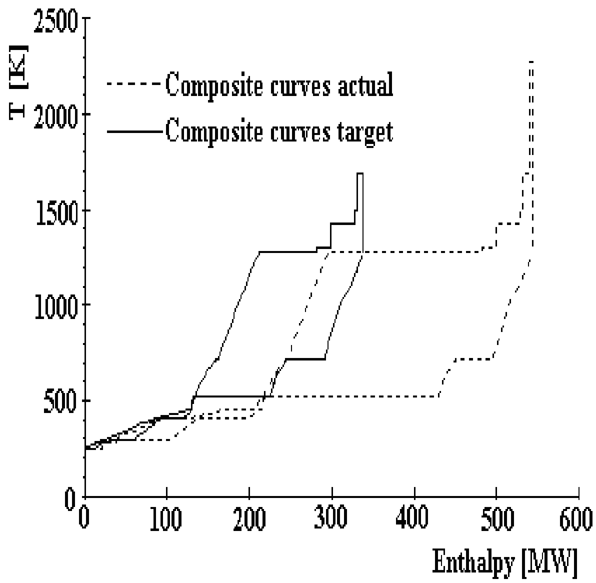

Figure 2. Balanced composite curves from CREI analysis

3. Chemical Reactor Analysis

Applying CREI analysis means, first of all, to compute whose departure from the actual working temperature gives the measure of the completeness of the chemical process and the quantity of the generated reaction heat. For the flowsheet at hand, temp is calculated using the zero-order approach, since all the chemical reactors are of RStoic type, as defined in AspenPlus® 11.1, thus being perfectly mixed. The chemical reactors from the network are replaced by their corresponding virtual heat exchangers. Six virtual utilities appear, each one at its own temperature . The extended heat exchanger network was presented to the pinch analyzer.

The returned topology was unfeasible, since nearly all the virtual pairs of hot and cold currents representing the chemical processes were decoupled completely, some other utilities being proposed instead. To overcome this drawback, largely discussed in a step by step procedure was followed. Instead of applying CREI methodology to all six chemical reactors simultaneously, only one reactor at a time was included in the analysis. After the CREI analysis taking into account only the first reactor, the new proposed topology was created. Then, the CREI analysis was applied to this new flowsheet, considering the second reactor, then, the subsequent ones.

In this way, the process should converge towards the optimum topology iteratively, and no possibility of interchanging two or more virtual utilities could appear. Nonetheless, at each step of the process decoding the topology is not a simple task, the engineering judgment playing a key role. The sequence of the reactors was arbitrarily chosen as PRIM-REF, SEC-REF, SHIFT-1, SHIFT-2, METANATO and AMMONIA (see Figure 1 for details). After considering the first reactor in series, the new topology emerged from the CREI analysis had an entropy production of 387.2 kW/K, significantly lower that that of the base case, but larger than that given by the PA. Applied to this new flowsheet, the CREI analysis gave, for the second reactor in series, an improved topology, with only 323.7 kW/K entropy generated (59% less than for the base case), better than after the pinch analysis. More, the total number of HEN units decreased to 42. The attempt of applying the CREI analysis for the rest of the reactors in series was unsuccessful, because, for every one of them, the pinch analyzer proposed the same basic variant: the virtual hot utility responsible for the chemical process, which had high virtual thermal potential due to the higher values of temperature, should be used for heating some cold currents situated at high temperature levels, while for the chemical process itself, some lower grade utilities were proposed. This cannot be done since it denies the chemical process itself, so the solutions were disregarded.

Due to the approximations made during the CREI analysis, when the actual chemical reactor is replaced by a virtual heat exchanger, and largely documented in a cascaded PA-CREI analysis should be envisaged, to obtain a better topology.

Different combinations of PA and CREI were analyzed. The flowsheet with the minimum of generated entropy was obtained for the cascade PA-PA-CREI. This topology generates 322.4 kW/K entropy. The improvement over the situation where only CREI was applied is insignificant (0.4%) but the number of units in HEN rose to 43. From an economic point of view, this could mean a raise not only in the investment cost but, also, in the operating one, since the pumping costs should, normally, increase. For the rest of topologies obtained during the PA or CREI analysis, the use of cascaded PA-CREI analysis gave no improvement.

6. Conclusion

The ammonia plant was modelled and simulated using AspenPlus® 11.1 of Aspen Technology, Inc. as simulation environment. Subsequently, a combined PA–CREI analysis was performed, to obtain a better conventional and chemical heat integration of this ammonia plant, searching not only for a better HEN arrangement, but, also, for better operating conditions for the chemical reactors. Due to the lack of intermediate utilities, between hot pressure steam (523.15 K) and FiredHeat (1273.15 K), the SuperTarget's Process® was unable to provide a satisfactory solution for the four reactors of six, when CREI analysis was applied; the pair of virtual currents encoding the chemical process was completely decoupled, the virtual hot stream (the provider of the chemical energy) being used to heat-up a high level cold current, while for the virtual cold stream (encoding the chemical transformation itself) a lower grade hot stream was proposed, thus turning down the chemical process.

7. References

[1] Penkuhn, T., Th. Spengler, H. Piichert, O. Rentz, 1997, *European Journal of Operational Research* 97, 327

[2] M.Appl, "The Haber-Bosch Process and the Development of Chemical Engineering" in "A Century of Chemical Engineering", *Plenum Publishing Corporation*, 1982, 20-51.

[3] Coulson and Richardson, *Chemical engineering third edition.Vol.6.* Butterwoth heinmann pub., 1999, 214-218.

[4] Ammonia Manufacturing Industry, EPA-450/3-80-014, *U. S. Environmental Protection Agency*, Research Triangle Park, NC, August 1980

[5] A.V.Slack,G.Russel james, *Fertilizer science and technology series-vol.2*, ammonia part 1, Marcel Dekker Inc,1973

[6] S.B. Thakore and B.I. Bhatt, *Introduction to Process Engineering and Design*, Tata McGraw Hill Education Pvt Ltd, New Delhi,