

Energy integration in ammonia production

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Abstract

Since its introduction by Haber and Bosch in the early twentieth century, the catalytic synthesis of ammonia from atmospheric nitrogen has become one of the worlds most important chemical manufacturing processes. Unfortunately, the process requires the use of significant amounts of energy, the European Fertilizer Manufacturers Association giving total average energy use per tonne of ammonia produced in 2000 as 37.4 GJ, EFMA [1]. If 1500 tonnes of ammonia per day is taken to be a typical plant output this represents an average power requirement of 649 MW. It is the reduction of this energy input that is currently being addressed by research at the University of Durham and Terra Nitrogen (UK) Ltd.

The paper will concentrate on the major processes that go to make up the industrial ammonia synthesis process as a whole and their interdependent nature. Examples of energy saving options will be given, focusing on the importance of using an integrated approach to avoid upsetting the sensitive energy balance. The value of using computer simulation as a tool to model process changes off-line will be discussed and the direct applicability of this work to other industries will be shown.

1 Introduction

Ammonia is synthesised at elevated temperature and pressure in a continuous process, using hydrogen obtained from hydrocarbon feedstock such as natural gas. Though the actual chemical process has remained largely unchanged, major step changes in plant output and energy use have been made through reconfiguring the energy balances and equipment efficiencies throughout the process.

The major step change to the process has been the introduction of centrifugal compressors in the 1960s, which opened the way for the large single stream plants now being built with capacities of over 2000 tonne/day, Nitrogen and Methanol [2]. The compressors could be driven directly by steam turbines using steam generated from process waste heat, the integrated nature of the process leading to greater efficiency. Plant efficiency became of great concern following the rise in oil prices in the 1970s leading to further process integration and optimisation in an attempt to reduce costs, resulting in the energy efficient designs of today.

There are large numbers of ammonia plants in Europe and North America built in the late 1960s and 1970s which have the potential to be highly energy efficient if modern developments in plant equipment and process parameters can be applied. Reduction in energy use through continued process optimisation is essential if these plants are to remain viable in the face of competition from new, more efficient installations being built in areas where energy prices are relatively low.

2 The ammonia production process and its major energy users

2.1 Reforming

The major input of energy to an ammonia plant is in the form of hydrocarbon feed, usually natural gas, which is reacted with steam in the primary reformer to produce hydrogen. The reforming reaction is strongly endothermic, requiring a large input of heat, which is provided by the combustion of fuel gas in the reformer radiant section.

Consumption of feed gas varies little between conventional ammonia plant designs, being in the region of 24.5 GJ/tonne, EFMA [3], which can be compared to the thermodynamic minimum energy of ammonia production of 22.5 GJ/tonne, Jennings [4]. Some processes such as the Braun Purifier operate with higher than usual feed gas rates of around 26 GJ/tonne, EFMA [3], relying on process heat generated by the feed stream after primary reforming to close the heat balance. It can therefore be seen that the major part of the effort to reduce overall plant energy use should be concentrated on the radiant heat demand of the primary reformer (reducing the amount of fuel gas consumed).

Most of the heat recovered from the primary reformer flu gas raises high pressure steam used to drive synthesis gas, process air and refrigeration compressors. A proportion of this steam passes out of turbines at an intermediate pressure and is mixed with feed gas to provide the water required for the methane-steam reforming reaction.

Primary reformer effluent passes to the secondary reformer where pressurised, preheated process air is added to provide the nitrogen necessary for ammonia synthesis. The gas temperature increases due to reaction with atmospheric oxygen, the higher temperature enabling the reforming reaction to continue to a point closer to equilibrium.

2.2 Purification

Before passing to the synthesis loop ("the loop"), the reformed gas must be purified to remove the CO and CO₂ produced as by-products in the reformer, these gases being poisons of the synthesis catalyst.

Carbon monoxide is difficult to remove, so instead is reacted with water, over a catalyst, to form CO₂ and more H₂ in the shift reactors. Removal of CO₂ is an energy intensive process requiring large amounts of heat and pumping power. Synthesis gas is passed through a pressurised column where it is scrubbed with an absorbent solution to remove the CO₂, the solution then being recirculated through the system after regeneration (removal of absorbed CO₂ from the solution). Regeneration is usually performed in two stages; flashing down to low pressure and then heating to drive off any remaining CO₂.

Before it enters the CO₂ absorber column the synthesis gas is cooled, the condensing process steam providing heat to regenerate the solution. If heat from the process stream is not sufficient for solution regeneration, additional heat must be supplied, usually via let down of high value steam, to complete the process. In older systems regeneration heat can account for 10% of the total energy needed per tonne of ammonia produced. Raising solution pressure after let down and circulating it around the system also demand a considerable amount of pumping energy, typical mass flow rates of solution being around 2000 tonnes/hr with a pressure increase in the region of 30 bar. Before introduction to the synthesis loop the gas passes through the final stage of purification, the methanator, where any remaining CO and CO₂ react exothermically with hydrogen to produce methane.

2.3 Synthesis

The ammonia synthesis loop operates at high pressure, often in excess of 200 bar, the main energy input being in the form of high pressure steam to the synthesis gas compressor. For a typical ammonia plant producing 1500 tonnes/day and operating with a loop pressure of 220 bar this compressor will have a demand in the region of 25 MW, some of which is required to circulate gas in the loop. In addition to the hydrogen and nitrogen required for ammonia production, synthesis gas contains small amounts of methane and argon ("inerts"), which are inert to the synthesis reaction, and traces of water and lubricating oil which are catalyst poisons. Water and oil are prevented from entering the converter by the introduction of make up gas to the loop upstream of the ammonia separator, allowing them to be carried from the system dissolved in the liquid product. The inerts build up in the loop, adversely affecting ammonia production by reducing the partial pressure of reactants and putting a greater load on the circulator. A purge stream must therefore be maintained to keep their concentration within set limits. The purge stream, though necessary, represents a material loss from the loop and the level at which it is set is critical to maintain plant efficiency.

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The synthesis reaction is exothermic, the heat produced (2.7 GJ/tonne) being equivalent to around 8% of that used by the process as a whole, and recovery of as much of this heat as possible is an important feature of the process.

In order to remove product ammonia from the loop, converter effluent must be chilled using a refrigeration system to condense the ammonia in the gas stream. The system, using liquid ammonia as the refrigerant, is normally driven by a steam turbine and rejects heat to the atmosphere from its condenser. This represents a large energy use directly related to synthesis loop operating conditions.

3 Options for the improvement of process efficiency

There have been many changes to ammonia plant design and operating conditions with a view to reducing energy use and increasing output, some of which can be applied to older plants relatively easily, and some of which are unsuitable without major structural and operational changes to the plant.

The change in attitude towards energy use in recent years can be illustrated by comparing design specifications for flu gas temperature between three ICI designed processes. The reduction in flu temperature shown in Table 1 represents the increased importance of energy recovery to the process. Increased heat recovery in this way comes at a price, with the LCA process using heat exchange coils constructed of corten to avoid corrosion from the condensing of combustion products at this low stack temperature.

Table 1: Comparison of ammonia plant design exhaust stack temperatures.

Plant	Year of Commission	Design Stack Temperature (°C)
ICI Ammonia 4	1977	175
ICI AMV	1984	140
ICI LCA	1988	110

Modern plants reduce primary reformer radiant duty and hence fuel gas use in a number of ways. The mixture of natural gas and steam fed to the reformer can be preheated to a higher level, using exhaust heat from the convection zone, with the effect that a greater proportion of the increase in sensible heat is derived from a lower grade. This shifts duty from the radiant section and allows a reduction in firing. Similarly, additional heat can be taken from the convection zone to increase preheat of fuel gas and combustion air.

The amount of steam mixed with the feed gas can be reduced, improving efficiency due to the lower amount of steam needed. Efficiencies are also gained due to the lower mass flow rate through the reformer, requiring less energy to heat it and drive the reforming reaction. Reduction in the amount of process steam is sometimes combined with an alternative source of supply. Instead of using steam passed out from a turbine drive, some systems use feed gas

saturation where low grade process heat is used to saturate the feed gas with process condensate. In addition to improving efficiency, the use of a saturator has the associated advantage of reducing pollutant emissions from the plant, pollutants such as ammonia and methanol in the condensate being taken up with the feed gas and destroyed in the reformer.

Though the reforming reaction is favoured by excess steam, low pressure, and high temperature, some modern processes are showing a trend to reduce primary reformer firing, thus reducing outlet temperature, Gu [5]. This is not an easy option for most older plants as the conversion of methane is significantly reduced, as is the amount of heat available for recovery to the process. Plants of this type shift more of the reforming duty to the secondary reformer, which has a higher thermal efficiency than the primary, by addition of excess process air (up to 50% more than is required for stoichiometric H:N ratio). A significant proportion of the un-reacted feed gas is combusted, raising the temperature sufficiently to drive the reforming reaction closer to equilibrium and make up the balance of process heat required. This accounts for the above average feed gas use of the Braun Purifier process.

Another consequence of excess air reforming is the need for a larger process air compressor, power for which may be unavailable within the plant energy balance. One solution is to use a gas turbine drive, using its exhaust as preheated combustion air for the primary reformer. Plants built in the past using this system can gain large efficiencies by replacing their old gas turbine with a new high efficiency model as demonstrated by Hydro Agri, Sluiskil, Versteel [6].

The most important feature of the process is the removal of both the excess nitrogen present (due to the increased volume of process air), and the relatively high concentration of methane (due to the mild reformer conditions). A cryogenic purifier system, the cold box, is used to adjust H:N ratio and remove methane immediately before entry to the loop. Modern purifiers can remove all methane and most argon from the synthesis gas resulting in a very low loop purge, high material efficiency and reduced compressor load. In addition, all moisture is removed from the gas stream prior to the cold box, allowing make up gas to be added after the ammonia separator. This reduces both the load on the refrigeration system and the ammonia concentration at entry to the converter thus increasing yield.

Retrofitting of a cold box purification system to more conventional plants is not a viable revamp option due to expense and differences in the overall process. Installation of synthesis gas dryers, however, with an associated change in the entry point of make up gas to the loop can bring about improvements in both efficiency and output.

Upgrade of the existing CO₂ removal system or retrofitting with a new low energy system is a popular revamp for older ammonia plants and can lead to a significant reduction in energy use if integrated with other measures such as lowering steam:carbon ratio. Care must be taken during selection of a system as there can be various knock on effects and unexpected problems leading to plant downtime and reduction of efficiency savings. Examples of this can be found in the cases of the "aMDEA" and "Selexol" CO₂ removal systems. The

manufacturers of aMDEA claim as an advantage over older systems the fact that the solution is non-corrosive. This may be the case for the actual solution but is not so for the activator used with it, a fact discovered at great cost by DSM Agro, Geleen. They changed over to the solution as part of an energy efficiency revamp and suffered severe corrosion problems as a result, leading to extended plant downtime and remedial work, Huurdeman and Goole [7].

Although it is true that some systems, such as Selexol, can be designed to operate with zero heat input, Verduijn and de Witt [8], this fact should not be seized upon as meaning that the system will operate without energy input. A major requirement of this system is for refrigeration, and in the case of an older plant looking for efficiency gains the refrigeration system is already likely to be a plant limit due to past capacity increases.

Efforts to reduce loop pressure by introducing highly active catalysts have resulted in some processes having very low synthesis compressor duty and reduced construction costs, Gosnell and Strait [9]. Adoption of low loop pressure is not however an attractive option for revamp of existing plants. This is due to the associated increase in refrigeration duty required to condense the product and the need for larger piping and vessels to accommodate the increased volumetric flow.

4 Importance of viewing as an integrated system

As with any energy intensive process, the importance of viewing the industrial synthesis of ammonia as an integrated system can not be over stressed. By its very nature, the first step in the process requires the input of huge amounts of energy in the form of high value heat. Much of this heat is not utilised for the purpose it was initially introduced, and must be recovered to other duties if an energy efficient process is to be maintained.

Gaining improvements in energy efficiency is therefore a complex issue; overall energy efficiency is controlled by the amount of fuel consumed to drive the reforming reaction, but reduction in heat input at the start of the process can result in energy deficiency elsewhere due to a lack of recoverable heat. Similarly, improvements gained elsewhere by such means as replacing old turbines and compressors with newer more efficient designs can result in a surfeit of recovered heat that may end up simply vented to the atmosphere. Some possible energy saving measures and associated effects on other areas of the process are highlighted in Table 2.

Increased mixed feed preheat temperature is a popular revamp option, Versteel [6], Ohri [10], although simply installing additional heat transfer area to the feed preheat coil is likely to upset the complex reformer heat balance. This could leave a heat deficit for such duties as steam superheating due to a combination of increased heat recovery and reduced reformer firing. The combination of these factors could result in increased auxiliary boiler firing to close the balance. To introduce the revamp successfully requires a complete audit of the heat recovery section and possibly installation of additional heat recovery surface to areas not requiring increased duty. Alternatively, if it is

found that increased preheat leads to a recoverable heat deficit, the possibility of replacing existing turbines and compressors with more modern higher efficiency units could be considered as a possible means of reducing steam demand.

Table 2: Energy improvement options and associated effects on the process.

Area of Plant	Improvement	Target outcome	Knock on effect
Primary Reformer	Increase feed preheat	Reduce radiant section duty and hence fuel requirement	Reduces heat available for other process needs
Primary Reformer	Reduce steam:carbon ratio	Reduce steam demand Reduce radiant section duty and hence fuel requirement	Increased methane slip Increased CO formation Reduced heat available for CO ₂ removal Increased loss of H ₂ in methanator Increased inert level in loop
Primary Reformer	Reduce outlet temperature	Reduce radiant section duty and hence fuel requirement	Increased methane slip, reduced heat available for other processes
CO ₂ Removal	Retrofit low energy system	Reduce heat demand	Process heat may be rejected to atmosphere
Synthesis Loop	Reduce loop pressure	Reduce compressor duty	Increase refrigeration load

Although reduction in steam:carbon ratio improves efficiency by reducing steam demand and reformer radiant duty, upset of the energy balance and downstream process changes can cause problems if the option is not carefully integrated with the plant as a whole. Lower levels of process steam can leave the CO₂ removal section with a heat deficit for solution regeneration, resulting in loss of efficiency due to the let down of high value steam, possibly generated via increased auxiliary boiler firing. Similarly, replacement or revamp of the CO₂ removal system with a more energy efficient system can yield lower than expected efficiency gains if the facility does not exist to reduce steam:carbon ratio, and thus available process heat.

The reforming reaction is favoured by excess steam, reduction in its quantity can result in increased methane slip and CO production, both of which have a detrimental effect on overall efficiency. Without the facility to reduce methane levels via excess air reforming or remove it prior to the synthesis loop with cold box purification, reduction in steam:carbon ratio can result in overall efficiency loss. Areas of inefficiency can include greater synthesis gas compressor duty and

higher levels of inerts in the loop requiring a larger purge stream with associated decrease in material efficiency.

The level of CO slip from the shift reactors, operation of which is favoured by excess steam, can increase with lower steam:carbon ratio. This can be compounded by the increased CO production from the reformer resulting in excess temperature rise and loss of hydrogen in the methanator and associated increase of methane entering the synthesis loop.

Though reduction of loop pressure gives the advantages of lower compressor duty and construction costs, application to existing plants is not an easy option due to a number of factors. Low pressure loops require use of larger equipment such as converter and piping, more highly active catalyst, which in the case of Kellogg ruthenium based catalyst is very expensive, and increased refrigeration to condense out product ammonia. Overall, increased refrigeration duty means that there is very little difference between the energy consumption of modern low and high pressure loops, Hooper [11].

The close integration between areas of the process mean that relatively small changes made in one area can have unexpected and unwelcome consequences for the plant as a whole. This is compounded in the case of adjustments of process parameters, which may exhibit an appreciable time lag before related changes become apparent. For this reason application of computer simulation is an ideal method for the consideration of plant revamp options and the adjustment of operating parameters. This will now be considered.

5 Computer simulation as a tool

The use of computer simulation means that possible changes can be modelled off-line without risk of adversely affecting the delicate plant balance and thoroughly assessed before application to the process.

This is well illustrated by the case of reformer outlet conditions, these having appreciable effects on all areas of the plant and being easily affected by operating parameters adjusted in an attempt to gain efficiency improvements. The time lag between adjustments made at the reformer and the change in gas composition at the synthesis loop mean that a large quantity of gas will have passed through the reformer before the overall effect on the plant becomes evident. This commits the plant to a period of operation under conditions that may be inefficient, and gives the risk of over correction when attempting to return to an optimum point.

If the same situation is modelled offline inefficient operating conditions are of no consequence. Any possible adjustment can be tried, and the computer model optimised by adjustment of variables such as purge rate until the most ideal operating conditions are found.

6 Direct applicability to other processes

The problems highlighted above and the application of computer process modelling are relevant to any industry where the process dictates a large input of

high value heat. It is at present impossible to recover heat at the level it is released by fuel combustion, with the result that any high temperature process based on combustion will produce more heat than is initially required, recovery and use of this excess heat being essential in the face of increasing energy cost and pollution tariffs. Any process relying on large amounts of recovered heat will by nature operate with a very sensitive energy balance, alterations to which should only be implemented when all available information and possible effects have been studied.

An example can be seen in the case of the energy integration programme applied to paper and board making in Finland, an energy intensive process that consumed almost 82 TWh in 2000, Siitonen and Ahtila [12]. Efforts to reduce CO₂ emissions by improved recovery of waste heat have resulted in the reduced possibility of plants producing electricity in their own CHP installations. Increased heat recovery has introduced the danger of higher energy costs due to greater use of bought in energy. This is compounded by the fact that bought in electricity is generated using fossil fuels, whereas that generated via CHP uses forestry waste, a renewable by-product.

7 Conclusion

Industrial ammonia synthesis is an energy intensive process relying on close process integration to achieve efficient operation. Energy costs are rising, new high efficiency plants are being built in parts of the world where energy is relatively inexpensive, and concerns over atmospheric pollution are increasing. Against this background plants built in the 1960s and 70s must strive for higher energy efficiency through greater process optimisation if they are to survive.

Many options for plant revamp and process optimisation have been developed which can be applied to older plants. For changes to be implemented successfully, however, requires an integrated approach that can be aided by application of computer modelling techniques.

This does not apply solely to ammonia synthesis but to any industrial process relying on the use of recovered heat for a major part of its energy, processes which have sensitive energy balances by nature. A tool, such as a computer simulation, that enables the examination of trial situations off line gives the process operator a great advantage in the selection of revamp options. Changes to process parameters within inter-related processes can therefore be optimised without risk of causing plant upsets that can be of great financial cost.

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