DESIGN YOUR LARGE AMMONIA PLANTS FOR STARTUP

By proper consideration of all operational requirements, shortages of steam and other startup difficulties met in earlier thermally integrated plants can be avoided.

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The emergence, since 1963, of the large steam ammonia plants in which all the large compressors are of the centrifugal type driven by steam turbines, and the plant self-sufficient in power and steam, has significantly assisted in the spectacular growth of the ammonia industry in the past 3 years.

However, the so-called "total energy concept" and the search to recover every calorie can bring with it, if one is not careful, a loss in flexibility and produce a plant with rather rigid operating characteristics which could prove in some cases to be relatively difficult to put into operation.

Almost independent plant.

One of the features of these large plants is that by using direct steam turbine drives, they can be made virtually independent of outside sources of electrical power. To achieve this end the process steam is generated at high pressure (1,500-2,000 Ib./sq.in. gauge) instead of 500 Ib./sq.in. gauge which is required for the process itself. Steam is superheated and let down through a back pressure turbine which drives the synthesis gas compressor.

The steam may be resuperheated at 500 Ib./sq.in. gauge to feed the steam reformer, and the remainder used in condensing turbines to drive process air, refrigeration, and synthesis gas helper turbines. In some cases there is a further steam pressure level used for smaller drives, pumps, ancillaries, etc. In other cases the smaller drives may be electric motors supplied by a steam turbine driven alternator or possibly by imported power.

Whatever the details of the system the general principle is that all steam driven turbines are supplied by steam raised in the plant itself. It does not require a great deal of imagination to realize that the balancing of steam requirements and steam production will be of prime importance from the point of view of ease of operation and control.

This problem is further complicated by the phenomenon of "surge" encountered with centrifugal compressors. The incidence of surge limits the throughput of a centrifugal compressor to a relatively high percentage of its full design throughput. As the steam production is in general a function of the percentage throughput of the synthesis gas plant, this virtually imposes a high limit on the turndown capacity of the plant. The synthesis gas plant however, can operate satisfactorily down to about 40% of design throughput and the centrifugal compressor could pass 40% of design gas by compressing, say 60-80%, and recirculating a large proportion back to suction. The steam requirement to drive the synthesis gas compressor may still be of the order of 60- 80% of full design load and as this is produced on the synthesis gas plant the steam production in effect limits the minimum turndown of the plant as a whole.

Ease of plant startup

The problem of turndown is also important in relation to startup of the plant. In an extreme case one could envisage a plant that once at 100% load would work very satisfactorily, but which would be absolutely impossible to start-up due to a pinch in steam requirements at say 60% of full load. This is the type of problem which has occurred in some plants of a type independent of outside steam and power supply.

Although the plant can finally be started up there is in most cases a period during which the steam balance is very tight. This period must be passed very quickly to enable the plant to start. The solution of the problem of course lies in the design office and not in the field.

Ammonia plants now, more than ever before, need to be designed with start-up in mind. The steam, and energy balances should be checked at all reduced loads and at all stages in the start-up of the plant, based upon a full knowledge of how these large plants are in fact put into operation. One way in which this can be done is illustrated by the following example.

Process description

Figure 1. is a base outline flowsheet of a typical 1,000 metric ton/day ammonia plant based on a feedstock of light naphtha; the synthesis loop pressure is 4,500 Ib./sq.in. gauge, with design inerts content of 13.5% in the circulating gas.

Feed is vaporized and preheated in a direct fired preheater followed by vapor phase desulfurization. The vaporized feedstock is mixed with steam and passed through the reforming tubes contained in a top fired reforming furnace, the outlet temperature of which may be in the range 1,450-1,550° F. Heat is recovered from the flue gas duct in a radiant shield boiler, process steam superheater, process air preheater, and a further superheater for the turbine steam. Final low grade heat is recovered by the preheating of combustion air. The flue gas is discharged via an induced draft fan to atmosphere.

Partial reformed gas passes on to the secondary reformer where the reforming reaction is carried a stage further, heat being supplied adiabatically by burning a portion of the gas with air. This process air is compressed by a steam turbine driven centrifugal compressor.

Heat is recovered in a waste heat boiler followed by high temperature shift conversion which has between stages a further high pressure waste heat boiler. The hot gas from high temperature shift is cooled for the second stage of conversion which uses low temperature conversion catalyst working around 400°F. $CO₂$ removal is typically by the steam regenerated Vetrocoke

Figure 1. Typical 1,000 metric tonday ammonia plant.

process followed by methanation for final removal of the small amounts of CO and CO₂.

The resulting gas is essentially a mixture of nitrogen and hydrogen, which is cooled and compressed in a centrifugal synthesis gas compressor to a pressure of 4,200 Ib./sq.in. gauge. By using this classical synthesis pressure a simpler plant results in that refrigeration is not required. This is only possible where cooling water is available at relatively low temperatures, otherwise the converter size becomes prohibitive.

The plant as shown has a relatively small steam raising load on the flue gas duct; i.e., only the steam necessarily raised from the radiant shield boiler, which is a desirable item for protection of the superheaters.

The balance of steam needed is raised on an auxiliary boiler but it could equally well be raised in the flue gas duct by employing auxiliary firing in the duct. However, an auxiliary boiler has definite advantages over extra flue gas duct steam raising surface mainly in the following:

- 1. Change of steam rate can be made more quickly.
- 2. Steam pressure control is easier and adjustments to the steam system operation can be made without affecting the furnace and the rest of the process plant.
- 3. Start-up is quicker and easier.
- 4. The auxiliary boiler can in many cases be fired with a cheaper fuel than the reforming furnace or flue gas duct.

Heat sources and steam uses

In ammonia plants steam is available from the following three main sources: (1) Heat recovery from process gas in waste heat boilers and boiler feedwater heaters, (2) heat recovery from the flue gas duct in a boiler and superheaters, and (3) an auxiliary fired boiler, (or extra flue gas duct equipment.

Figure 2. Steam-turbine system in a typical plant.

Steam users are shown in Figure 2, but basically they are: (1) For driving turbines for the synthesis gas makeup compressor and circulator, process air compressor, and turbo alternator plus other drives as required, (2) as process steam reformer, and (3) for regenerating in the carbon dioxide removal plant.

Design considerations

Full load and reduced load operation. The following factors are used in estimating a valid steam and power balance for the plant:

- 1. Determination of synthesis loop characteristics at all loads.
- 2. Matching the makeup gas compressor and loop circulator characteristics to the synthesis loop conditions at various capacities, and estimating the corresponding power requirements and compressor speeds.
- 3. Determination of power and steam demands for other sections of the plant at all loads.
- 4. Calculating the total heat required for raising steam needed to produce the power required by the compressors and other power users as obtained in 2 and 3 above.

For each condition the auxiliary boiler capacity needed to supply any balance of steam is determined and the installed capacity includes a safety margin in excess of the maximum demand at whatever load this maximum demand arises. The margin is chosen depending on the efficiences of the turbines included in the design and allowances are made for considerable fall off in efficiency of compressors and turbines during the life of the plant.

Startup operation.

Critical operating conditions occurring during start-up should be fully analyzed with respect to heat availability and power demand. For instance the process air compressor requires a certain quantity of steam for starting. Before air is available the reaction in the secondary reformer does not proceed. The contribution to steam production by the waste heat boiler after the secondary reformer is therefore less. Therefore, almost the whole of the steam to drive the air compressor is supplied by the auxiliary boiler.

The following points must be considered at each phase of startup:

- 1. The startup will be carried out within previously tabulated parameters. Unless startup is checked it can be limited by the capacity of operation of the auxiliary steam system.
- 2. All electrical power loads of individual users to be evaluated at all working conditions.
- 3. All steam loads and major steam users to be characterised and appropriate safety margins allowed on anticipated figures.
- 4. Finally, full steam and power balances should be derived for all stages in the startup. This ensures, at the design stage, that the steam production capacity installed is adequate. It also provides detailed information of the situation at all stages in the startup which enables all the startup operations to be pre-programmed. It, in fact, provides the basis for a full startup simulation probably some 18 months before the plant is complete and ready to go.

A greater percentage of the power and steam demands of the plant is readily available from characteristic curves etc., but the power and steam requirements at reduced load of the synthesis gas compressor/circulator require special study. The following method is used to determine this.

The amount of ammonia produced in the synthesis loop is a function of: Catalyst activity, pressure, circulation rate, inerts content, and temperature of the cooling medium.

Most plants are designed on the basis of catalyst activity at the end of a 2-yr. life. Therefore we can fix this variable as the plant must equally well be capable of starting up and operating towards the end of its catalyst life.

It can be seen in Figure 3 that synthesis gas compressors can be started when the synthesis gas section is working at about 60% based upon 2-yr. old catalyst. With new catalyst the compressor

could be started at a lower percentage at full load by using a correspondingly lower synthesis loop pressure. Therefore, during the first year of operation for instance, a plant could be run quite economically at 50 to 60% full load and without having to recirculate gas around the compressor. This flexibility to operate at reduced load is often an advantage when an operator has a market not fully developed at the time of installing of the plant.

The cooling temperature used in the design is 60° F which is considered average for more temperate regions.

If a non-refrigerated loop is considered we are, therefore, left with three variables that can be changed to some extent independently. However, there is still a certain amount of interdependence between production rate, pressure and circulation rate as normally the circulator is run off the same shaft and, therefore, at the same speed as the makeup gas compressor.

As control of the makeup gas compressor is best obtained by variation of its speed, it can be seen, Figure 3, that for a given makeup gas rate (or production rate) at a fixed loop pressure there is a fixed compressor speed. This, therefore, fixes the circulator speed and the circulation rate. A limited variation is possible within this range by the use of inlet guide vanes if fitted, although it is doubtful if a case can be made for fitting guide vanes to the circulator.

Detailed steps in the calculation

The following detailed steps should be taken in carrying out the calculation:

First, take a given percentage of full load operation and calculate the makeup gas rate corresponding to the production rate for a chosen inert level in the loop. The second is to assume a number

Table 1. CALCULATED POWER CONSUMPTION OF SYN. GAS COMPRESSOR AND CIRCULATOR AT REDUCED AMMONIA PRODUCTION RATES

Table 2. POWER & STEAM REQUIREMENTS

Figure 4. Rotor with recycle and synthesis impellers of the last casing of a centrifugal compressor for a 1,100 metric ton/day ammonia plant.

Figure 5. Last casing of a centrifugal compressor for a 1,100 metric ton/day ammonia plant ready for assembly.

of synthesis loop pressures. For each pressure then obtain the compressor speed from the compressor performance curves.

Using this speed, the third step is to obtain from the circulator characteristic curve the circulation rate and the pressure at the inlet of the converter. From the circulation rate and pressure then calculate the make of ammonia.

The fourth step involves repeating the above until the calculated make equals the assumed make. The result of this analysis is a table which gives the makeup gas compressor and circulator speed and power consumption for various loads, as shown in Table 1.

Having obtained the data for this section of the plant the balance of the steam/power requirements are calculated. The complete steam production for any particular pLase of startup or reduced load is then tabulated. This is shown in Table 2.

Example calculations

I would now like to illustrate the above outlined procedure by following through this example. The flowsheet used is that shown in Figure 1, and is considered to be a self contained unit i.e. does not input steam or power for start-up.

Full load operations: By considering flowsheet values, the total steam to be supplied by the auxiliary boiler is determined.

Process heat available at full load:

Total 484.0×10^6 Btu/hr.

The steam is reheated after passing out from the first turbine at 500 lb./sq.in.gauge from 610° F to 900° F (enthalpy change = 162 Btu/lb.).

Total steam produced is 418,000 Ib/hr. Therefore total heat required:

 $(1393+162)$ 418,000 = 650 \times 10⁶ Btu/hr.

Therefore the heat to be supplied by the auxiliary boiler or auxiliary firing:

 $(650 - 484) \times 10^6 = 166 \times 10^6$ Btu/hr.

Startup: Similar steam and heat balance calculations will be done for each critical stage in the start-up. The choice of operating conditions for each critical stage will be based upon previous knowledge of the way in which this type of plant is, in fact, started up.

Stage 1 involves reduction of the low temperature conversion catalyst, and to start the auxiliary boiler using standby drives, e.g. diesel engines.

Reduction of the low temperature catalyst entails the following: Pressurization of the plant to about 85 lb./sq.in.gauge with nitrogen and circulation of a mixture of hydrogen and nitrogen around the plant using the process air compressor. (The second stage only of the 2-stage centrifugal will be used). At the same time various ancillaries will be operating i.e. instrument air compressor, mixers and service pumps for $CO₂$ removal solution make-up, etc., and it is probable that the $CO₂$ removal circulating pump will be in continuous operation circulating water or dilute solution for cleaning.

Power required:

22ÖÖKW

900° F.

Process air compressor second stage, only 1,000 KW *Steam requirements:* At this stage in the startup there is no useful contribution to steam production from the process. All steam must come from the auxiliary equipment:

Therefore load on auxiliary boiler: - 57 \times 10⁶Btu/hr.

Stage 2: Heating the plant is the next step involved. After reduction of the low temperature conversion catlyst, the converter is bottled up and left under nitrogen. The whole plant is pressurized to above 300 lb./sq.in.gauge with nitrogen and circulation is started. The feedstock preheater and furnace are ignited and plant heating commenced. The temperature is increased slowly to about 1,300° F outlet the furnace tubes. At this temperature steam is admitted and slowly built up to around 90,000 lb./hr. Hydrogen is now bled in to start reduction.

Stage 3: Commencement of reforming is the next stage. Feedstock is added and slowly increased in rate. Nitrogen circulation is cut. Plant load buildup to about 40% of design throughput (steam carbon ratio for normal operation is 3: 1 molar. At this load during the first startup we shall be using about 4: 1 as a precaution against accidental carbon deposition due to any unsteadiness during start-up. $CO₂$ removal plant will require low pressure steam from pass out turbines.

Stage 4: At about 40% load, the secondary reformer will be brought on line. The amount of air put into the secondary reformer initially will be low, about 25% of full load. But the air compressor work very near to surge and, therefore the amount of steam required to drive it will be a much higher percentage of the full load requirement. In this case approximately 70% of steam of full load requirement is used in the calculation, this being on the safe side as the possible reduction in discharge pressure has not been taken into account.

Steam requirements for this are:

Stage 5: Volume of secondary air quantity is slowly increased until it is in correct proportion to the gas flow. Instruments are checked and then the steam ratio reduced to approximately the design value. The whole plant throughput is then increased to 60% of full load and the boiler pressure slowly increased to the full working pressure of 1,500 Ib./sq.in.gauge. At this point the synthesis gas compressor will be put on line.

By referring to Table 1, which shows the calculated power consumption of the sythesis gas compressor and circulator at reduced production rates prepared as previously outlined, the total power for a particular load is available. Using this figure and the other steam consumption given in Table 2 the total steam to be raised is thus determined, as follows:

As additional heat will now become available from the process due to the synthesis reaction, the auxiliary boiler load will reduce. This calculation does not take into account the initial phase of synthesis catalyst reduction which would not normally take place at as high a pressure as 60% load operation and therefore would not use as much steam.

Reduced load

As can be seen by the above example the load on the auxiliary boiler at reduced capacity is available from the total steam requirements given in Table 2 and the heat available from process. An example of this is at 60% load:

As full load auxiliary capacity is 166×10^6 Btu/hr. the other reduced load requirements, will lie between these values and are

Q. You spoke of safety margins which should be added on for less than design efficiency of turbines or a loss of efficiency of turbines. We also had difficulty, particularly in naphtha reforming plants, with safety margin associated with such things as waste heat boiler fouling. I would like to hear some comments as to what these margins ought to be. I know in one case the 10% was not enough.

N1MMO: We would use on auxiliary steam capacity a figure of about 20%. On boiler fouling we utilize a fouling factor approximately four times the original fouling factor used in the design of these plants. This results in an increase of boiler surface of approximately 20-25% and gives adequate control of temperatures entering the shift converter.

Q. Have you investigated the synthesis gas compressors to be operated at 4,700 Ib./sq.in.?

NIMMO: Yes, our mechanical engineers have studied this very carefully and witnessed test of the final barrel. However, we do not offer this higher pressure necessarily and do incorporate other machines at slower speeds, depending on the particular circumstances. The Italian compressor has been tested in Italy and the first unit will be coming on stream in 1968.

Q. In the statement on safety margins, was the 20% margin on the auxiliary boiler on the total steam requirement basis?

NIMMO: The 20% is purely on the auxiliary boiler capacity, based on the maximum demand as calculated.

Q. When you have different pressure levels for steam, what do you recommend for auxiliary boiler pressure level?

NIMMO: We have incorporated both the higher pressure and medium pressure boilers in our designs. The medium pressure level results in a slight loss in over-all efficiency. However, by having a medium pressure level a large sink of steam is available for the reformer which is an operating advantage. We would favor a medium pressure boiler, if the economics were reasonable.

not critical. The following tabulation shows the various heat loads on the auxiliary boiler:

As can be seen from the above analysis the critical point in the start up comes when the air compressor is put on line. This emphasizes the need to fully consider these factors in the design stage of the plant.

In order to allow latitude in the design for initial performance of compressors and turbines being less than anticipated, for reduction during operation of compressor and turbine efficiencies, and for process upsets and control margins the auxiliary boiler should then be provided with additional margin of safety. This procedure then results in an adequate steam supply for startup and a flexible plant will be the result.

Conclusions

The inflexibility of the earlier large thermally integrated ammonia plants can be largely avoided at little cost by considering all the operational requirements, including startup and reduced load, operation during the design stage.

The steam system should adequately cater for the following: (a) Critical phases of the startup, (b) less than expected efficiencies of the large compressors and turbine, (c) fall off in compressor and turbine efficiencies with time, and (d) reduction in ammonia synthesis catalyst activity and the consequent need to start up at higher loop pressures.

With properly designed plant it is possible to operate economically at between 50 and 60% of design ratio during the first year.

Discussion

Q. Starting up your high pressure synthesis gas compressor would still be a problem would it not?

NIMMO: This can be overcome by installing additional condenser capacity in the low pressure stage to help the turbine.

Q. Could any of the turbines or compressor manufacturers give us their opinion on declining performance of this equipment with age? Is there any statistical experience.

H.A. WIEGAND, Ingersoll-Rand: I think the concept of a steady decline of performance with age is totally wrong. We have units running at well over 2000 psi for over 10 years. There has been no noticeable decline of capacity. If there is wear or erosion you will get a loss of efficiency but this may not necessarily be tied directly to age. It can come about during a short period of misoperation where a rub may take place and a sudden increase of internal leakage results.

FRANK HUNTER, Cooper-Bessemer: There is another point to consider and that is the degree of moisture separation between centrifugal compressor casings, particularly in the synthesis gas train. We know that good separation is a must with reciprocating compressors. It is also a must with centrifugal units since there is a definite possibility of rotor erosion if the liquid separation between centrifugal casings is not adequate.

ATWOOD, Worthington: From a turbine viewpoint deterioration will depend largely on the purity and quality of steam going through the turbine. Dropoff will depend on degree of erosion in buckets and nozzles.

E. NOBLES, Mississippi Chemical Corp: We ran into a very dangerous situation with failure of oil seal equipment on our new centrifugal refrigeration compressors. Notice shoud be taken of this situation by all firms with centrifugal compressors using ammonia in the manufacture of ammonium nitrate. The situation was as follows.

In our centrifugal refrigeration compressor, failure of one gasket in the oil seal system caused seal oil to flow directly into the body of the compressor. This unexpected occurrence in a few minutes put many barrels of oil into the ammonia vapor of the refrigeration system. This oil mixed with the ammonia and promptly passed out into the product stream proceeding thence to the ammonium nitrate plant. At the nitrate plant slugs of oil carried through into the neutralizer. Fortunately, we were able to spot and correct this situation before trouble although some brown nitrate did result.

Thus, a particular oil seal failure in this compressor can result in the catastrophic explosion that our entire industry must avoid. Our corrective steps included:

a. Placing separators in the refrigerant vapor system.

b. Placing separation storage capacity in the ammonia pro-

duct stream.

- c. Provision of vaporization equipment in nitrate neutralizer feed.
- d. Addition of oil separators in urea offgas lines.
- e. Addition of oil absorptive filters on ammonia line to neutralizers.

We at Mississippi Chemical will be willing to assist others with this problem.

ANON: I think the seal you are talking about is a contact carbon ring seal and there is no question the situation you note could occur. But with the fail-safe oil film seal, this could not happen.