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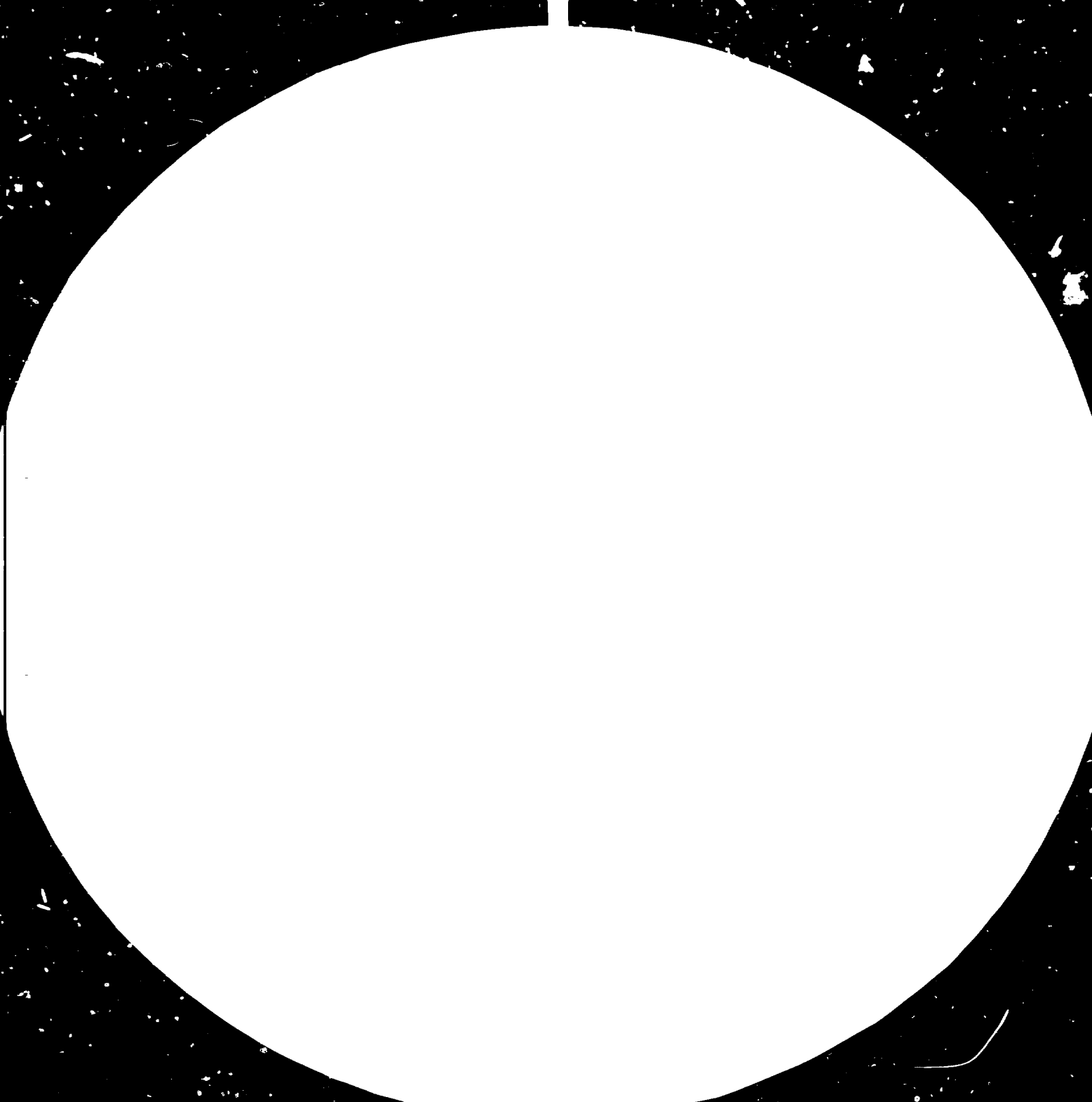
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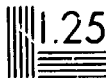
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ENERGY CONSERVATION IN AMMONIA PLANTS*

by .

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Since 1900, world population has quadrupled from 1.000 million to the current level of 4.400 million. The Malthusian catastrophe has been avoidable only by the use of revolutionary agricultural methods including the use of man-made fertilisers, in first place nitrogenous ones.

Food and with it fertiliser availability is one of the major problems facing most developing countries. Their Nitrogen demand, estimated to 18,1 million tons of N in 1980 is expected to rise up to 55 million tons in 2000. But although nitrogen in its free form is very abundant in the atmosphere; 77.000 tonnes over every hectare of the earth's crust, to fix out of this only the amount necessary to give a good crop on one hectare roughly 8 GJ must be spent. So it is no wonder that the whole history of the ammonia industry is a history of energy efficiency and so is its future too.

Despite continuing efforts to find radically new methods of producing chemically combined nitrogen, no economically or technically superior industrial method to chemical ammonia synthesis can yet seriously be said to be in prospect.

The sixty years old ammonia synthesis process was the first industrial high pressure catalytic process converting large amounts of energy. Starting from an overall thermal efficiency well below 20%, with over 90 GJ/to N through a steady and spectacular technical development it reached in the fifties a high technical level at 66-68

GJ/to N and an efficiency considered as very high by that time. In the early 1960's a revolution in the ammonia plant design took place with the introduction of the large scale single stream integrated flowsheet with a very high degree of energy recovery. The energy consumption fell to 44-45 GJ/to N corresponding to an efficiency of around 50 %.

It is interesting, for two reasons, to make a detailed investigation how it was possible to achieve such a tremendous improvement: first to find out, how these results could be used in the quite different conditions of the developing countries and the equally different economic situation prevailing now and in the foreseeable future; second to evaluate the possibilities for future improvement and development trends.

Until a few years ago it was taken for granted that a modern ammonia plant to be economic must be as stated above: large scale, single stream, integrated with maximum heat recovery and based on steam reforming of natural gas. And if we consider the flowsheet of such a plant /Fig 1./ and its energy recovery system /Fig 2./ we can only agree.

A. Energetic aspects of a modern ammonia plant

Among the basic energetic features of the modern ammonia plant, the most fundamental factor is pressure, although others, such as the raw materials /hydrocarbons, especially methane/ and

mechanical achievements /construction materials and equipment/
the elimination of separation process /except carbon dioxide removal,
and more efficient carbon dioxide wash systems, also have a con-
siderable contribution.

Raising the pressure in synthesis gas production and steam genera-
tion had two main effects: it enabled large-scale production in a
compact, single-stream process unit with an integrated, highly effi-
cient heat recovery system and it enabled compression power require-
ments to be reduced considerably.

Energy recovery

There is a very high degree of heat recovery /Fig 2./. Close in-
tegration provides for heat exchange between areas of surplus and
demand. A large part of the waste heat from the flue and process
gases is used to raise high-pressure steam of about 100 bar. Super-
heated to over 500 °C, and expanded in a back-pressure turbine to
the steam reformer inlet pressure produces some 300-350 kWh/to N.
Thereafter, steam surplus to process requirements is used in con-
densing turbines to make up the difference between power require-
ments of the main compressor train and the output of the back-pressu-
re turbine. Low cost centrifugal compressors took the place of the
formerly used electrically driven machines; their lower efficiency
is more than compensated by their lower price, lower maintenance
cost, greater reliability, smaller space requirements and the use
of expansion energy derived from waste heat instead of costly
electricity.

An important part of the heat content of the process gas is in the form of the latent heat of the steam excess. This heat can be utilized industrially only at a reasonably high temperature level. Fig. 3 shows how decisive the pressure is from this point of view. With a pressure of 30 bar, nearly 60% of the total latent heat can be recovered at over 130 °C, while at 10 bar no condensation can occur at all above 146 °C, and at atmospheric pressure the dew point is 78 °C and so practically no recovery is possible. The total latent heat of the water vapour in the gas corresponds to 16-17% of the total energy input; compared with a total loss, a recovery with 60% efficiency of this heat improves the overall thermal balance of the whole ammonia plant by about 10%.

A considerable contribution to plant efficiency has been made by modern carbon dioxide removal units. Chemical systems such as the activated potash or MEA-DEA systems, using less heat in a two-step scrubbing operation, are in wide use today. The major part of the dissolved carbon dioxide is released simply by depressurizing; only that part of the solution used in the second scrubbing step has to be steam-stripped. Just recently, interest has grown in the physical solvent type of process, in which no regeneration is required and the CO₂-rich solvent is regenerated merely by depressuring.

The recovery of 85% of the reaction heat from the synthesis loop is a further improvement in the energy balance.

Savings in compression work due to steam reforming under pressure,

in the production of 1 tonne of nitrogen for 1 bar pressure increase in gas manufacture are:

10,3 kWh/tonne N/bar between	8-14 bar
5,3 kWh/tonne N/bar between	14-21 bar
2,4 kWh/tonne N/bar between	21-35 bar
0,85 kWh/tonne N/bar between	35-49 bar

The disadvantage of the elevated reformer pressure is that there will be a higher residual methane content unless the temperature or the steam : carbon ration in the steam reformer or both are increased.

The effect of higher residual methane content on total energy consumption is presented in Fig. 4 for various reformer pressures and two inert gas contents in the synthesis loop feed.

The end point of the compression is set by the synthesis pressure. The lower this is, the lower will be the make-up gas compression work but the higher the compression work for recirculation and ammonia condensation. So there is an optimum value, but this is always specific to the given conditions. Figure 5. is an example for a given set of parameters.

Energy balance and opportunities for conservation

To assess the possibilities left in such an integrated process for further energy conservation, it is necessary to examine the energy balance in some detail. There are several ways to do so: the total energy flow, the energy balance /Q-t/ diagram and the work lost balance. One example of each type is presented here.

Figure 6. shows the total energy flow for the whole process: 49% of the energy input is accountable as the heat content of the product.

Figure 7. shows a Q-t diagram for the steam reforming heat recovery system only.

Table 1, summarizes the work lost from the different units of the whole process.

When looking for energy conservation two possible courses can be followed:

- Revision of the classical flowsheet
- Investigating new flowsheets.

Revision of the classical flowsheet

Primary steam reforming furnace

The thermodynamic efficiency is high: 87-89%, the energy recovery system very elaborate. Nevertheless, 55% of the total work lost is concentrated here /Table 1./, and so the biggest irreversibility also /Fig. 7./ . The main causes are the big temperature differences, the highest being in steam generation /about 600 °C/.

With present and foreseeable possibilities, there is little hope of changing this situation substantially, but a few percent can be recovered in the following ways.

Preheating air for the burner. This raises the overall efficiency to 91-93%. A 25 °C reduction in the stack temperature is equivalent to a 1% efficiency gain /with 15% excess air and 2% radiation losses/, and so 600-700 MJ/tonne N can be saved. A flue gas temperature at the stack of 150 °C gives a combustion efficiency of over 92%. It is perfectly feasible technically to reduce the stack temperature to 100 °C, especially where /sulphur-free/ natural gas is being used as the fuel. But the size of the combustion air heater has to be increased by 60%, and the extra investment can seldom be justified.

Secondary reformer

The second highest contributor of "work lost" is the secondary reformer and its waste boiler. This is due to the combustion of air in the secondary reformer and the large temperature difference between the secondary effluent gas and the steam generation temperature, and here also major improvements do not seem feasible.

Carbon dioxide removal

The single classical separation step remaining in the process still uses heat for regeneration, but at a low level furnished by the last stage of heat recovery from the synthesis gas, so a better carbon dioxide removal system, consuming less or no heat, must be tied together with some new means of utilizing the low-level heat saved.

Compressors and drives

Nearly 20% of the total energy for ammonia production goes into compression. Under operating conditions in the normal range, typical operating efficiencies of the machines used are approximately as follows.

Centrifugal	70%
Condensing turbines	25%
Back-pressure turbines	70%

If both compressors and turbines were improved to the currently understood limits, then it is possible that power requirements could be reduced by 3-4 MW for a 1,000 t/d ammonia plant, equivalent to about 100 kWh/tonne N, or 800-1,000 MJ/tonne N.

Synthesis loop

In the ammonia loop, most modern processes recover about 2-3 MJ per tonne nitrogen. It would be possible to increase this by 20% only with rather heavy extra investment.

New flowsheets

Every process owner in the world is busy at the moment with R and D work aimed at new and more efficient steam reforming flowsheets. Many papers and patents have been published and, although there are as yet few commercial or even semi-commercial realizations, one can already discern the basic features in the new tendencies.

The classical reforming process is, in every respect, well and delicately balanced. Not only are the process steps carefully matched on the one hand and the energy surpluses and demands well balanced on the other; the two aspects are also closely interwoven. The combined hydrogen and heat balance corresponds to primary reforming up to a methane leakage just equal to the quantity which can be eliminated in the secondary reformer by the heat input coming from the air carrying the necessary amount of nitrogen; methane leakage from the secondary reformer is held to the minimum possible; shift conversion efficiency is maximized; carbon dioxide removal is highly efficient. All this is in order to minimize the inerts content after the methanator and to maximize hydrogen utilization efficiency, reaching the 93-95% level.

If attempts are made to reduce substantially the heat requirement for the reformer /the main energy consumer and entropy producer/, there will at once be less HP steam and low-temperature waste heat. To maintain the balance, process steam, driving power and low-level heat requirements have to be reduced in parallel - and that is basically what everyone is trying to do now, in spite of the apparently different approaches. How can this be done?

Purge gas recovery

Beginning at the end, with the purge gas: effective action here can obviate the need for improvement earlier in the process train. Thus, if the purge gas is processed by one of the several different methods /pressure swing adsorption, cryogenics or diffusion/ to recover the valuable component /hydrogen/ and /possibly/ argon as a commercial by-product, logically there is no longer any reason

to strive for a low inert content in the synthesis gas. The first thought is to reduce the steam:carbon ratio. Better, more active catalysts are sought and simpler schemes worked out. The HP steam requirement can be reduced either by using a gas turbine drive, a very powerful change /instead of steam consumption, steam generation occurs by more fuel consumption/, or by using absorption refrigeration in the loop in place of the refrigeration compressor. Even the oldest method /due to Haber/ of removing ammonia from the loop by absorption in water /instead of condensation/ combined with absorption refrigeration is under active consideration. Minimizing power requirements by means of better machines, or of better catalysts which lower the required necessary synthesis pressure, or of new converter types with low pressure drop and high productivity, or of higher reforming pressures - these are some of the more obvious corollaries of pursuing this particular track.

High purification of synthesis gas

Another approach is to alter the purification train to deliver extra-pure synthesis gas to the synthesis loop, reducing the purge to a minimum and at the same time relieving the severity of the reforming furnace duty. If, for example, a PSA or a cryogenic unit is inserted as the last stage of synthesis gas purification, very high-purity synthesis gas can be produced from a rather high-methane, high-CO content gas, the fraction containing these impurities being diverted to the burners of the primary reformer. In this case, the primary reformer can be run under less harsh conditions, there is no need for secondary reforming, and only HT shift conversion is needed - a much simpler production

but it must be completed by a PSA unit and pure nitrogen is needed because, without a secondary reformer, no air is introduced into the system. This nitrogen has to come either from an external source or from a specially provided air separation unit. If an air separation unit is provided, a cryogenic /liquid nitrogen wash/ separation system can be used instead of a PSA system.

The need for a separate source of nitrogen is the principal disadvantage of this strategy; for, unless nitrogen of adequate purity happens to be available as a by-product of another process, the additional investment, relatively poor efficiency and high power requirement of an air separation unit tend to offset any economies made in the ammonia plant. There is one system, however, that produces a highly pure synthesis gas without recourse to a separate nitrogen source while still retaining the advantage of reduced severity in the primary reforming furnace, but without dispensing with any of the process stages of the conventional plant. The Braun Purifier process removes all the methane remaining at the primary reformer outlet by secondary reforming, and the excess of nitrogen resulting in the process gas is then removed as a liquid containing all other residual contaminants, including methane and argon, leaving a pure stoichiometric mixture of nitrogen and hydrogen.

It will be apparent that the feasibility of any of these options is dependent on the balance between many variables, and this is affected by the relative importance that is attached to them in each case: for example, the respective importance of saving energy and minimizing costs. So for every case not only must a complex process

and energy balance be worked out but an economic optimum as well. The different proprietary processes differ in this very point - how they put the individual building blocks together to find their optimum.

Possibilities for developing countries

Over a hundred plants all over the world have been built to the "classic" process scheme described and most of them with great success. Nevertheless some bitter experience especially in several developing countries casts a heavy shadow over this bright picture. Delays in construction and start up, overruns of initial budgets, low on-stream factors, operational difficulties, maintenance problems more than offset the potential economic advantages. The feedstock market and transport situation in many developing countries is anyway strongly adverse to the erection of jumbo plants. So it seems highly interesting to examine not only the future improvement possibilities but also whether the economic advantages of this process scheme could be severed from its undesirable features - big size and oversophistication.

A detailed study shows that it is possible to build a modern ammonia plant with not much lower economic and energetic efficiency but medium or small sized and less sensitive.

The modern ammonia process by itself is simple, easily controllable and can be implemented in any size. The economic and energetic advantages of the process are independent of size. For capacities under about 600 t/day NH_3 only reciprocating compressors can

be used. These are more expensive need more maintenance, but have higher efficiency and are less demanding in technical service. So the specific investment cost of a smaller plant will be higher but otherwise will be not less modern or less efficient.

Another aspect is the whole energy recovery system. First of all there is a close relationship: the higher the energetic efficiency, the higher will be the specific investment cost - independently from the size of the plant. The difference is that for a big plant even relatively small energetic improvements will result in big sums of money, so there is a big incentive to recover every joule. For a small plant it can be more interesting to have a simpler plant easier to operate and a higher on-stream factor and accept a somewhat lower energetic efficiency. Raising steam at medium pressure only e.g. will result in a higher energy consumption but all the troubles with feedwater quality, boiler turbine and expansion valve operation will be eliminated.

The economics of ammonia production are often treated in a somewhat misleading way. Most calculation are for ideal cases, not for real ones:

- the specific investment figures, the curves representing the investment cost in function of the capacity refer always to battery limits only. The additional costs however /utilities, infrastructure etc/ amount to 50% and in the case of the developing countries up to 100% of the battery limit costs. These

costs in many cases cannot be represented by a continuous curve; local availabilities and limitations can introduce big stepwise changes and in most cases, lower utilities and infrastructure costs of a smaller plant can offset the higher battery limit costs.

- all specific energy consumption figures and production economics are based on 330 days of uninterrupted operation at full capacity. Or if frequent shutdowns occur, energy consumption will raise by 20-30%, a substantially higher figure than the whole benefit from a sophisticated heat recover system.

- the fertiliser consumer has to pay not only the manufacturing but also - among others - the transportation costs. Or, in the developed countries, the transportation adds about 10% to the energy consumed in the factory. For trans-ocean shipments, freight add 20-25% to the f.o.b. costs but in remote locations upto 100% or even more can be charged for transportation. So in remote locations in spite of higher initial costs and even higher running costs a smaller and less sophisticated local plant could be competitive with imported product from an advanced jumbo p' .

All above reasons lead to a simple, in principle well known but not always applied conclusion: in every actual case, let it be in a developed or developing country, no principles or general rules should be followed but by a detailed feasibility study the energetic and economic optimum should be defined.

Energy is a key factor in the ammonia and fertiliser business. Therefore it is necessary to consider it without any prejudice. Energy can be saved by building new, big very efficient plants, by revamping existing production units but one should not overlook the possibilities offered through efficient fertiliser marketing and use. A study of the International Fertilizer Development Center /Energy and Fertilizer, Policy Implications and Options for Developing Countries/ stated: "The most promising means for saving fertiliser energy is more efficient use at the farm level". And I would like to emphasize that for a developing country where expanding food production to meet the need of the growing population is of paramount importance, the two key factors: fertiliser and energy should be subject of a careful and extensive sector planning and receive high priority. In this planning however, against all the decisive role of the energetics, the last word should be given to the economic results.

Fig. 1.: Process Flowsheet of an Integrated Ammonia Production Process

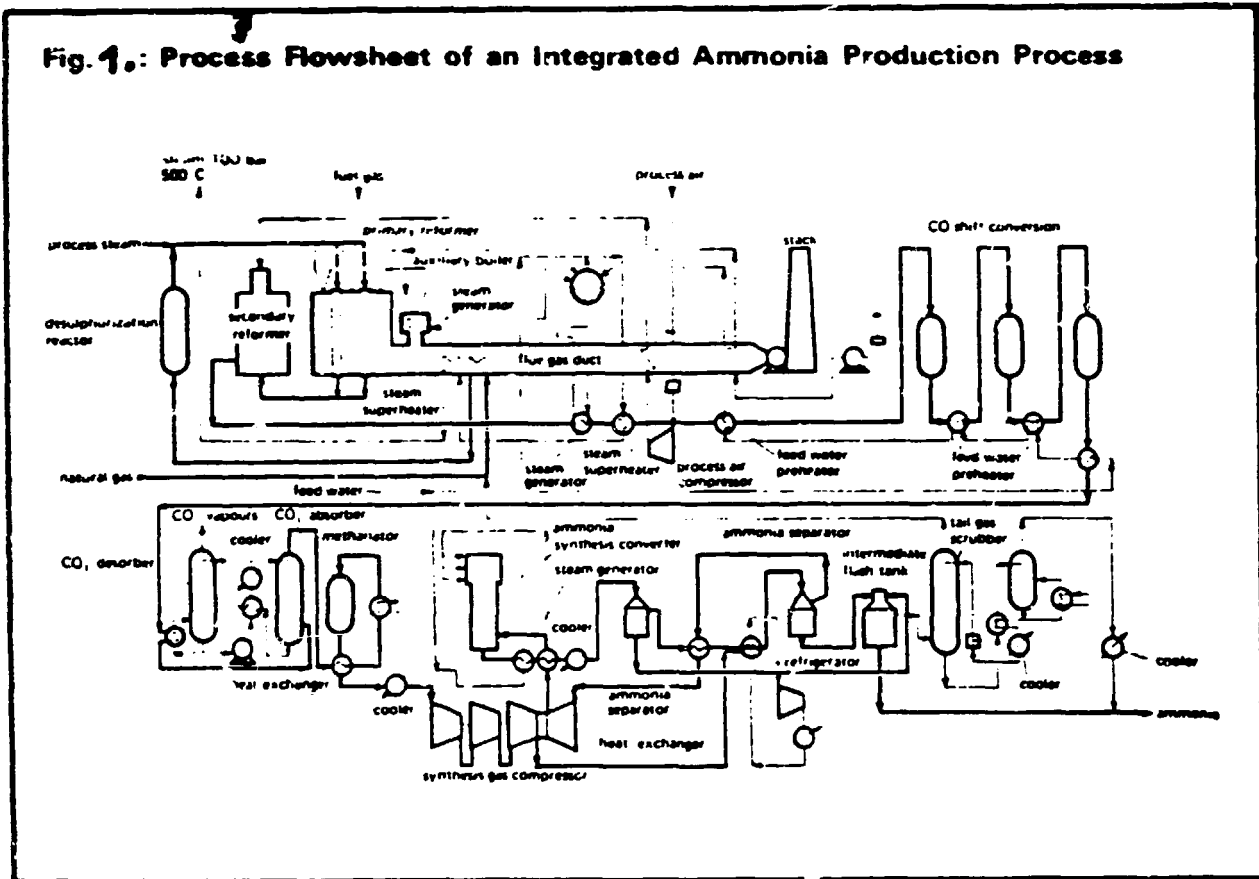


Fig. 2: Energy Recovery System for Process of Fig. 1

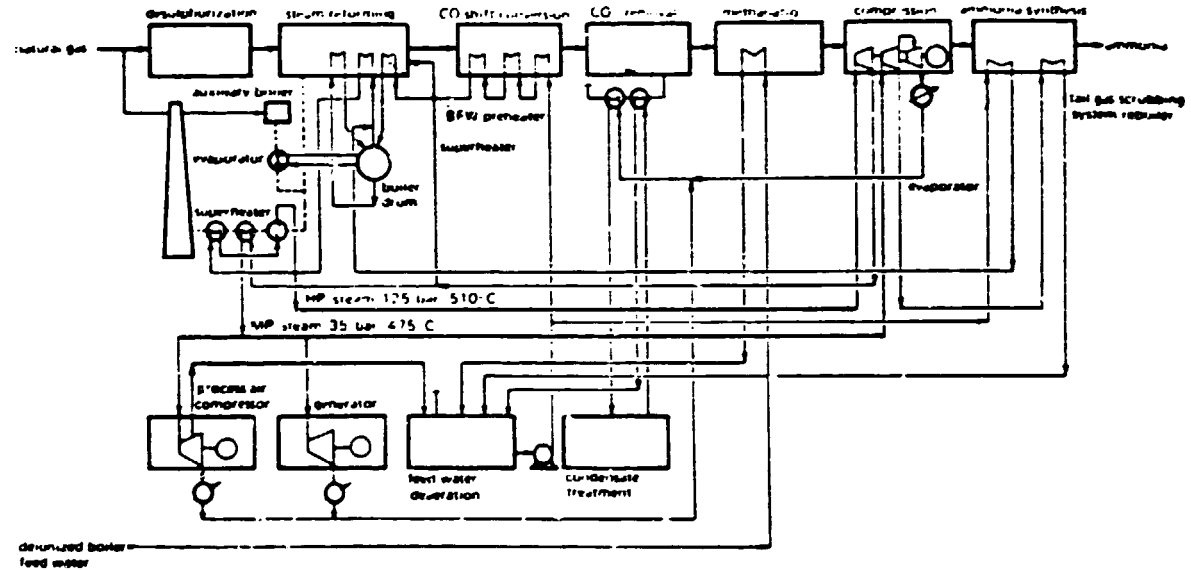


Fig. 3 : Quantity of Heat Recovered by Steam Condensation from Saturated Synthesis Gas

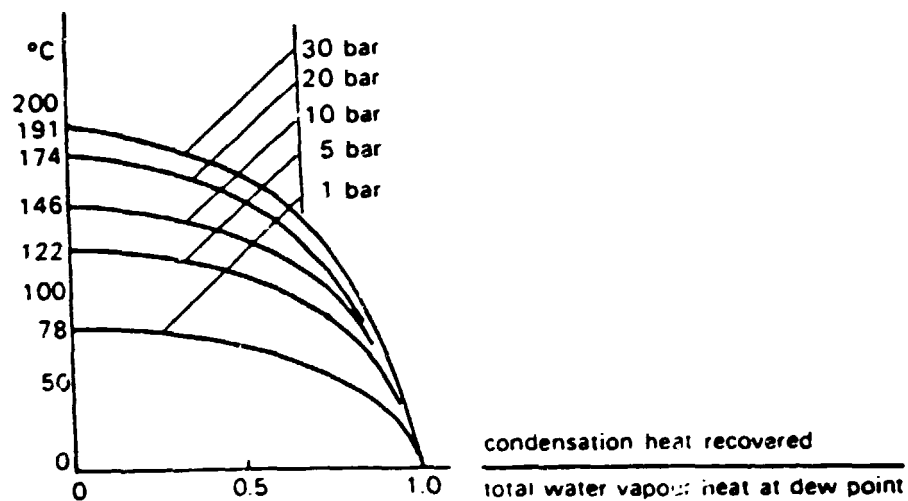


Fig. 4: Effect of Loop Feed Gas Methane Content on Compression Energy Consumption for Various Reforming Pressures and Two Loop Inert Levels

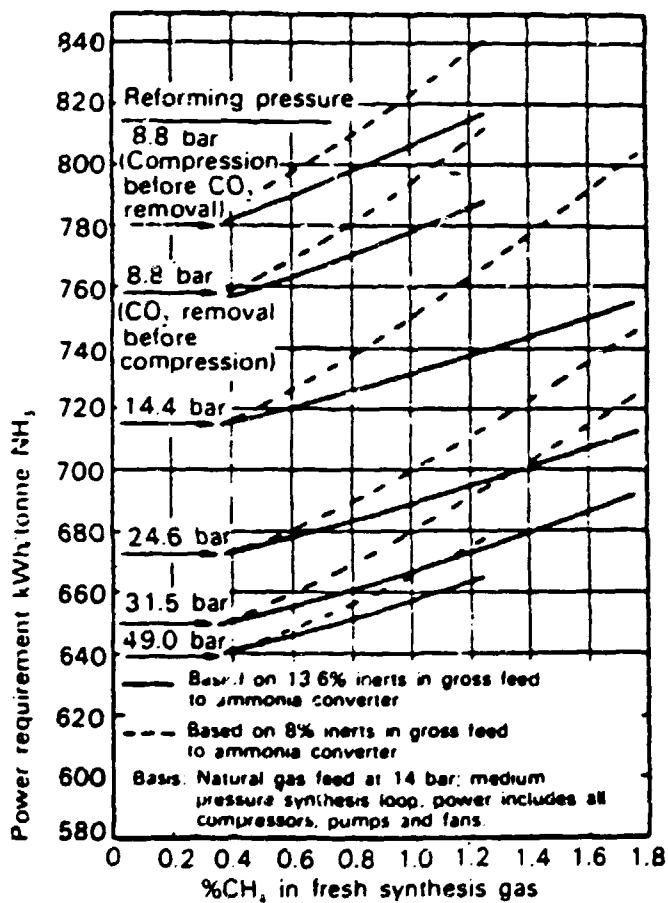


Fig. 5 : Effect of Synthesis Pressure on Compression Power Requirement (900 t/d NH₃) (after Appl)

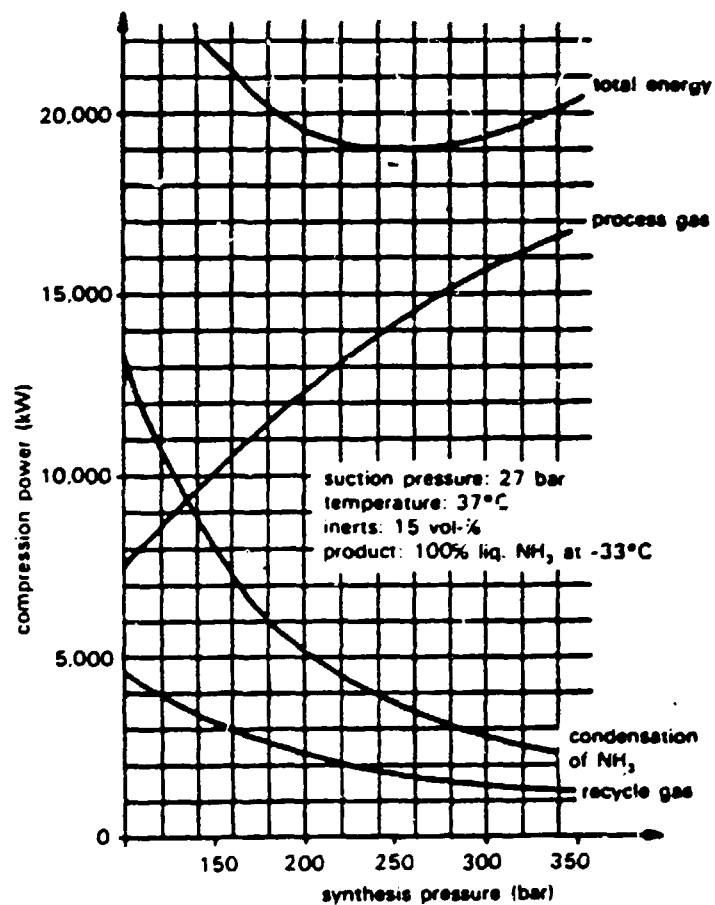


Fig. 6 : Energy Flow Diagram of 1,200-t/d Ammonia Plant Based on Natural Gas Steam Reforming. (Figures are MJ/tonne NH_3 .) (After Appl).

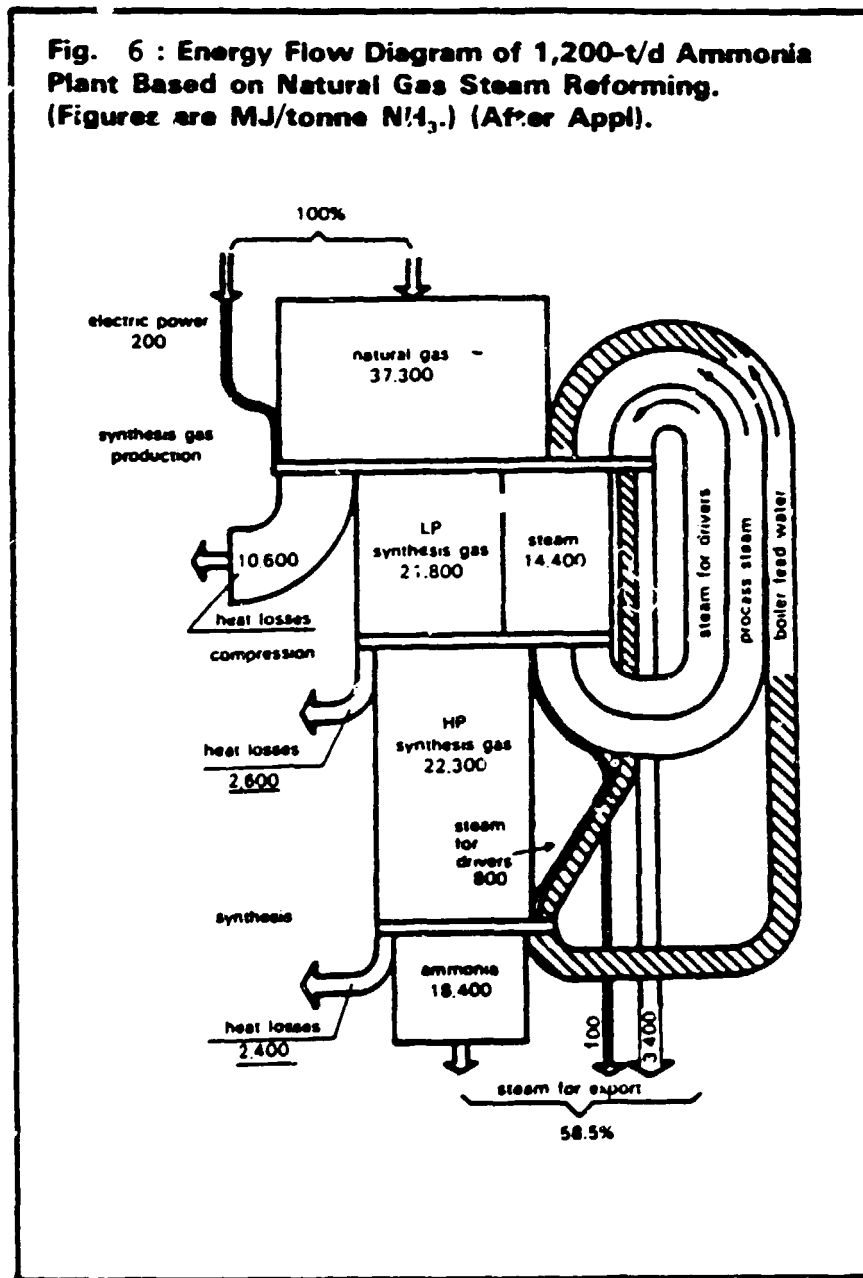


Fig. 7 : Q-t Diagram for Heat Recovery System in Steam Reforming

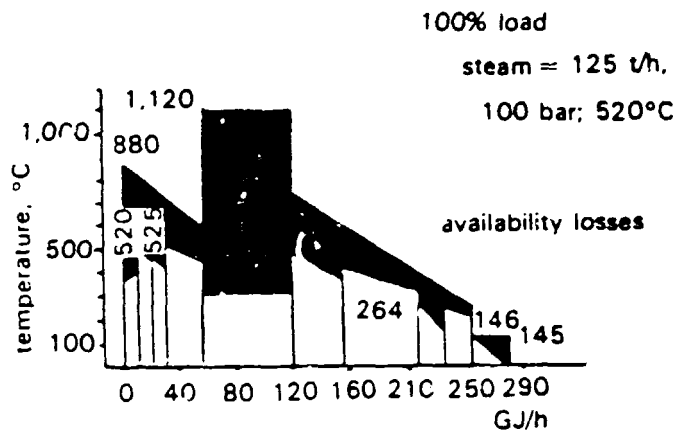


Table 1
Work Loss from a Natural Gas-Based Ammonia Plant

Area description	Work lost GJ/t	Work lost as a function of total work lost from the plant, %
Preheat and primary reforming (with flue gas waste recovery and steam generation from auxiliary firing in the flue gas duct)	10.17	55.0
Air compressor secondary reforming and waste heat boiler	2.55	13.7
High and low temperature shift and methanation	0.54	3.1
Carbon dioxide removal	1.09	6.1
Compression and synthesis	1.55	8.4
Plant refrigeration	0.12	0.8
Steam system	1.55	8.4
General losses	0.84	4.5
Total	18.41	100.0

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