International
Fertilizer Industry
Association

IFA Technical Conference

Venice, Italy

2-4 October 1990

THE ICI LEADING CONCEPT AMMONIA (LCA) PROCESS

D. KITCHEN AND A. PINTO
ICI Catalysts & Technology Licensing, United Kingdom
[illegible]

INTRODUCTION

Over the past century the world has seen a great increase in population, and this has intensified the need to produce food in greater quantities with increasing efficiency. The demand for nitrogenous fertilisers has grown correspondingly.

Right up to the late 1960's this demand was satisfied mainly by small ammonia plants, but with the development of the total energy concept for ammonia technology the industry started to build larger plants to meet the increased demand (Figure 1).

During the period 1965-1985 the traditional size of an ammonia plant rose steadily from 300 to approximately 1350 metric tons per day. Large tonnage plants have been the "norm" in the ammonia industry for the last two decades. This pattern is typical of a rapidly expanding commodity industry, but advantages of economies of scale force designers to adopt increasingly more difficult manufacturing and construction techniques. The construction and operation of such plants imposes increasing stresses on the local environment and infrastructure.

It is unlikely, however, that the past rate of growth of nitrogenous fertiliser production can be maintained. The Food and Agriculture Organisation (FAO) data show a slow down in the rate of growth of world fertiliser nitrogen consumption (Figure 2). This reduction in the growth rate of demand for nitrogenous fertilisers, coupled with monetary constraints and a need to minimise the impact of new plants on their locality, has created a demand for smaller ammonia plants.

The demand for new process technology has recognised a growing environmental awareness. New process designs are required to eliminate or reduce drastically gaseous and liquid emissions to meet the anticipated environmental standards of the future.

In 1983 market forces demanded that ICI's two oldest and least efficient ammonia plants; located at Severnside, near Bristol, England; be replaced. The fertiliser production site had been built around these two plants which produced a total of 900 te/day of ammonia. The obvious solution of building a single, large plant would lose many of the considerable advantages of flexible two plant operation. On the other hand, however, capital and efficiency penalties traditionally associated with small plants seemed to rule out multiple units. An analysis of ICI's possible replacement and expansion programmes for the future demonstrated that cost effective small plants would have many advantages compared to larger units.

ICI therefore, decided to develop new technology to improve the economics of small scale plants to those achievable in the best large plants, and to operate with the highest environmental standards. The result of this development is the ICI Leading Concept Ammonia (LCA) process.

Ammonia production from hydrocarbon feedstocks involves four major processing steps:

1. Feed pretreatment
2. Steam and air reforming of hydrocarbons
3. Gas purification
4. Ammonia synthesis

With conventional ammonia technology, high energy efficiency is only achievable by complex and integrated heat recovery between these processing steps. This energy integration leads to extended and expensive start-up times and major operational and control problems.

The LCA concept on the other hand uses an innovative and imaginative approach to decouple the process steps and eliminate the complicated interactions and interdependencies.

This paper describes the LCA concept for ammonia production and demonstrates how this novel design approach results in considerable benefits and enhanced operational flexibility.

- rapid start-up
- reduced start-up energy requirements and costs
- faster, more efficient shut-down procedures
- minimised gaseous venting during start-up or under upset conditions
- flexibility to operate efficiently at reduced rates
- considerably reduced effluents
- simplified control
- easy integration with other processes

By separating into a "core" unit only those key operations essential to making ammonia, and incorporating steam/power generation, ammonia refrigeration and CO_2 recovery into a separate "utilities" section, the LCA concept offers not only excellent opportunities for efficient site integration of a new plant, but also effective expansion or replacement of existing ammonia plants.

PROCESS DESCRIPTION

A flowsheet of the ICI Severnside LCA plant is shown in Figure 3.

Natural gas feed is mixed with recycle hydrogen, heated and desulphurised. The gas is then cooled, by preheating the feed to the desulphuriser, before passing to a feed gas saturator where it is contacted with circulating hot process condensate. This supplies approximately 90% of the process steam. The feed gas from the saturator is mixed with a further quantity of steam to give a steam to carbon ratio of about 2.5, and preheated by the reformed gas stream. Reactants enter the primary reformer, which operates with an exit temperature of 700-750°C and a pressure of 30-45 bar. The exit gas mixture is fed to a secondary reformer for further reforming with an excess of process air. Effluent gas is cooled by providing the heat for the primary reforming reaction and preheating the reactants. The cooled, reformed gas is shifted in a single, isothermal, low temperature shift converter. After shift conversion, the gas is cooled by direct contact with circulating process condensate, and fed to a pressure swing separation unit to remove the excess of nitrogen, CO_2 and some of the inerts. CO_2 can be recovered from the pressure swing separation waste gas using an aqueous solution of tertiary amine, but this is not an essential part of the ammonia production process.

The gas leaving the pressure swing separation unit is methanated, cooled and dried before entering the ammonia synthesis loop at the circulator compressor suction. Gas from the circulator is heated and passed over a low pressure ammonia synthesis catalyst to produce ammonia.

The hot gas leaving the ammonia converter is cooled by generating 60 bar steam (the only point in the process where steam is raised) and by heating the feed gas to the converter. Ammonia is separated from the partially cooled gas by vaporising liquid ammonia, and unreacted synthesis gas is recycled to the circulator.

Argon and methane are removed from the synthesis loop by taking a purge and recycling back to the synthesis gas generation section as feed.

MAJOR PROCESSING STEPS

The individual process steps in the LCA process have significant advantages over more conventional plant designs.

Feed Pretreatment

Conventional HDS systems require temperatures in excess of 370°C, a temperature that cannot be attained with steam heating, and has to be carried out using a source of heat at elevated temperatures. The most common approach in conventional plants is to use the primary reformer flue gas as a source of heat. This energy integration introduces constraints on plant start-up which cause both delays and energy wastage.

In the LCA process hydrodesulphurisation of the feed natural gas is carried out at a temperature below 250°C; a temperature which is achievable using process steam. The LCA process, therefore, eliminates considerable delay and energy usage during start-up.

The PURASPEC low temperature desulphurisation process gives significant capital cost savings, and allows a fast and energy efficient start-up of the hydrodesulphurisation section independently of the reforming section. (PURASPEC is an ICI trademark).

Steam and Air Reforming of Hydrocarbons

Primary reforming of steam and hydrocarbons is an endothermic reaction with the heat requirement traditionally being provided by a thermodynamically inefficient combustion process. Typically only 50% of the heat generated is transferred to the reaction, leaving the remainder as waste heat which has to be recovered through a costly and thermodynamically inefficient system.

Air addition and secondary reforming by contrast is an extremely exothermic reaction overall, and subsequent waste heat recovery from the effluent gas at around 1000°C is achieved conventionally by expensive and inefficient power/steam generation.

In the LCA concept, by contrast, the heat generated in the secondary reforming reaction is utilised to provide the endothermic heat requirement of the primary reforming reaction. There is direct heat exchange of the two gas streams in a tubular, gas-heated reformer (GHR). By changing the dominant heat transfer mechanism from radiant to convective, a compact pressurised GHR provides the optimum capital and energy utilisation solution to what was previously the most cost intensive and energy inefficient processing step in ammonia production.

Start-up of a conventional reforming section is a lengthy process requiring a number of steps, many linked to commissioning the plant steam system, which result in excessive feed and fuel wastage. A LCA plant GHR/secondary reforming section can be brought on line in a single step operation.

A feature of the LCA reforming section is the absence of a conventional multi-burner reformer, this eliminates the need to stabilise operation at high throughputs during start-up. On a traditional plant it is necessary to achieve good feed distribution between the tubes and to avoid overheating by careful burner control. There is thus no possibility, on the LCA plant, of the catastrophic melt-downs experienced in a number of conventional tubular reformers on start-up; and a GHR can be safely operated at as low as 15% of flowsheet rates while remaining process equipment is commissioned.

This simultaneous GHR/secondary reformer start-up method combined with much reduced rates greatly reduces the time to bring the plant on line and reduces the amount of energy wasted by venting.

There are improved safety aspects around design and operation of the LCA reforming section. Because the GHR operates with a very low differential pressure across the tubes, stresses are very low compared to those in the conventional reformer and creep life of the tubes is probably longer than the plant design life. In the very unlikely event of a tube failure, some gas will pass directly to the secondary reformer effluent resulting in a small increase in methane slip from the reforming section. As the shellside gas is oxygen free, there is no danger of a leak firing in the GHR and a tube failure will have little effect compared with a leak in a fired furnace.

Loss of hydrocarbon feed to a conventional reformer requires a trip of process air and a reduction in primary firing. In the LCA process feed and air supply are interlinked and failure of either automatically trips the other, resulting in a safe plant shut down. With hot re-start achieved in only 2-4 hours, the LCA process provides safer and faster recovery from plant upsets than any other operating process.

Gas Purification

Use of robust and self-adjusting process units in this section of a LCA plant makes it much less sensitive to catalyst performance and process upsets.

The single isothermal shift converter eliminates the need for an expensive control system. The reaction heat is transferred directly to the saturator circuit, contributing to the provision of process steam for reforming. This single stage efficient isothermal shift concept greatly reduces start-up time required compared with conventional two (and occasionally even three) stage shift systems.

The ability to utilise a copper catalyst in this duty facilitates energy efficient reforming at a low steam : carbon ratio (2.5), without formation of hydrocarbons by Fischer-Tropsch reactions which can occur over conventional iron-based high temperature shift catalysts.

The pressure swing separation unit performs a number of functions:-

i CO_2 removal

ii control of the $N_2 : H_2$ ratio by removal of excess nitrogen

iii removal of a proportion of CO, CH_4, Ar

The use of pressure swing separation makes the process much less sensitive to the performance of the up-stream catalysts. It can be fully automated, and requires much less time to bring on line than the conventional wet CO_2 removal systems and cryogenic excess nitrogen rejection systems which have been eliminated. It also cushions the synthesis area of the plant from feed gas disturbances.

Ammonia Synthesis

ICI has considerable experience with low pressure (80 bar) ammonia synthesis, and as applied in the LCA process the main additional advantage is the reduced start-up power requirement. The synthesis loop can be started in parallel with synthesis gas generation thereby contributing very significantly to reduced start-up time.

PROCESS FEATURES

The LCA features outlined in the Introduction are all of direct practical advantage to the plant owner, and have been incorporated into the plant design and proved in operation.

The process steam is largely self controlling as 90% is raised by internal recycle in the feed gas saturator. The recycle system is stable and buffered by its own capacity. This also meets the requirements to minimise effluents as these are recycled back into the reformer and destroyed.

The GHR operates at a steam ratio of 2.5:1 to minimise energy requirements and improve the economic performance of the plant. In conventional flowsheets this would give problems with hydrocarbon formation over a standard iron based shift catalyst. The lower operational temperature of the single stage LCA shift reactor allows the use of a copper-based shift catalyst which eliminates any possibility of hydrocarbon formation.

The CO shift conversion is achieved in a single stage, which eliminates one of the major vessels and waste heat recovery systems used in conventional designs and gives excellent control of the catalyst temperature. The reaction heat is recovered directly by the recycle condensate on its way to the saturator, without the need for a boiler and associated steam system.

The only boiler in the ammonia-producing core unit removes heat from the ammonia synthesis loop. Steam is raised at 60 bar which is superheated at Severnside to 450°C in the utilities section. There is no need to raise steam at high pressure and temperature as is common in conventional ammonia plants, thus avoiding the operational problems associated with this type of equipment.

The product gas from the pressure swing adsorption unit imposes a very easy duty on the methanator and process gas drier, which reduces the likelihood of poisons affecting the synthesis catalyst.

Fast start up and easy control are facilitated by operating the hydrodesulphuriser and methanator at temperatures that can be attained with a steam heater. This eliminates the need for a fired preheater and the normal process gas preheater before the methanator.

PROCESS CONTROL SYSTEM

There are three fundamental controls inherent within the LCA process scheme:

- steam : carbon ratio is controlled by adding approximately 90% of the process steam through natural gas saturation and then using a subsequent trim addition to about 2.5

- process air rate is directly linked to the secondary reformer exit temperature
- strict control of the $H_2 : N_2$ ratio in the make-up gas is achieved by adjusting pressure swing separation cycle times on an individual bed basis.

The simple, decoupled nature of the LCA process scheme makes it possible to automate start-up, normal operation and shut-downs extensively.

The control system on the ICI Severnside LCA plant consists of a Taylor Mod 300 system, a Sattcom computer and PLC's. In addition, a hardwired system, it's reliability independent of the main control system, provides safety trip protection. Non-safety trips are programmed into the control system.

Automatic start-up sequences have been written for a number of plant operations (Figure 4), and the structure of a typical sequence is shown in Figure 5.

Automatic shutdown sequences have been written for all equipment with start-up sequences, as well as key plant trips. As an example the structure for the shutdown sequence for the Severnside turbo alternator is shown in Figure 6.

The advantages of such sequences are the same as those for start-up ie reliable, repeatable and cost effective operation. In addition they will switch off certain alarms that are not required after the equipment is shutdown. This reduces the number of unnecessary, distracting alarms the operator handles at shutdown.

Use of this high level of automation not only allows rapid and cost effective start-ups and subsequent optimised operation, but significantly enhances the operational reliability the unit. With a minimum requirement for external manipulation of the plant, a maximum of 3 operators per shift is required for the complete 900 tpd complex plus utilities at Severnside and these manning levels do not require supplementing for start-ups or shut-downs.

OPERATIONAL AND DESIGN FLEXIBILITY

Operation

Previous mention has been made of the rapid, low cost start-up capability of the LCA units from cold. The second Severnside plant was commissioned in a world record time, making ammonia just 19 hours after introduction of feed gas. Subsequent cold restart has been achieved in only 12 hours, with a future target to reduce this to less than 8 hours. Following a trip, production can be re-established in only 3-4 hours for a hot restart and in future it is expected this time can be trimmed to only 2 hours.

This experience compares with typical start-up times for conventional units of around 20 hours (accelerated low energy start-up) or 50 hours (conventional start-up). With the reduced venting rates during the LCA start-up cycle, saving in gas wastage alone compared with a world scale unit start-up are estimated at 1475 GJ (31,000 million BTU), without taking into account the added value of additional beneficial ammonia production achieved by an LCA plant.

The ability to start-up rapidly and cheaply allows the adoption of a different philosophy opposite operating problems; and with LCA it will often be more cost effective to shut-down and repair equipment, rather than limp along accepting process limitations as may happen on a conventional larger plant.

A feature of normal operation is the high turn-down ratio achievable on the running plant. LCA units can be operated effectively down to 70% of design rates, enabling plant output to be adjusted to market demand where required. Further turn-down to rates as low as 15% of flowsheet is possible, with only a small penalty on the overall gas efficiency.

Design

By separating the basic steps for ammonia manufacture into the reproducible 'core' unit, the 'utilities' section can then be adapted to meet the specific individual customer requirements. This allows an excellent opportunity to optimise a complex site operation and integrate with downstream processes such as urea in the most effective manner.

Total process feed and fuel energy requirement for the LCA process is less than 24.4 GJ/Tonne (21 million BTU/ton) of product and this offers the flexibility to choose the most cost and energy efficient power cycle and fuel for on-site generation or, alternatively, the option to import.

CO_2 recovery is not essential for ammonia production and the LCA concept allows the freedom to match this to specific customer requirements. An operator who has no need for the CO_2 does not need to recover it, while there is sufficient CO_2 available for the conversion of all the ammonia to urea if that is the requirement.

As the main processing steps are decoupled, they can be used separately or in appropriate combinations for debottlenecking and improving efficiency on existing units, or for stage wise modernisation and upgrading of the facilities.

INTEGRATED MANUFACTURE OF UREA

LCA is a most effective ammonia plant for the integrated manufacture of urea. The process inherently produces more CO_2 than required for total conversion of ammonia to urea.

Ammonia processes based on methane have an idealised material balance:

$$7\ CH_4 + 10\ H_2O + 8\ N_2 + 2\ O_2 \dashrightarrow 7\ CO_2 + 16\ NH_3$$

They are therefore 12.5% short of CO_2 to convert all the ammonia to urea. Higher hydrocarbons in the gas reduce the problem but do not solve it. The normal design solution to produce extra CO_2 is to burn a hydrogen rich stream after CO_2 removal, usually the loop purge. This is not efficient in energy or capital usage.

As the heat of reforming in an LCA process is provided by the combustion of methane with excess air there is therefore more CO_2 available in the process stream. Only about 90% CO_2 recovery is needed to supply the stoichiometric requirement to convert all the ammonia to urea.

For CO_2 recovery from the waste stream the partial pressure exit the pressure swing absorber is about 0.15 bara, which would compare with a maximum of 0.07 bara on a conventional process with CO_2 removal to low levels prior to methanation. A simple and low cost system can therefore be used, and ICI have carried out feasibility studies based on a number of CO_2 removal systems.

In examining the advantageous integration of LCA with urea it is not particularly important which urea process is chosen as modern processes have very similar energy requirements and material efficiencies. There are some differences in the detail of the energy balance but they are minor in effect.

Figure 7 demonstrates a typical integration. This shows one LCA plant and one urea plant. For a urea plant of this capacity an electric drive is sensible for the CO_2 compressor in view of its cost and reliability.

The site power and steam demands are supplied by an integrated gas turbine and steam turbine power cycle. This scheme is similar to the recent low energy flowsheets where the air compressor is driven by a gas turbine and the other main drives are driven by steam turbines. The layout constraints in offsites power generation are more favourable for construction and maintenance than direct drives. The independent boiler system allows steam to be raised at startup for both the ammonia and urea plants. The offsites can be commissioned in advance of the main process plant which minimises maintenance turnaround duration and restart times after a main unit trip.

ENVIRONMENT

The LCA technology has been designed to achieve the highest environmental standards. This has been recognised by the award to ICI of the 1989 Better Environment Award for Industry for its LCA process.

By eliminating the atmospheric combustion of fuel in the primary reformer, the only NO_x produced is where waste gas is burnt at low temperatures in the process air preheater, the utilities boiler, and the converter start-up heater which only operates infrequently.

Net reduction is around 87% as shown in the comparative figures below for UK natural gas based processes.

	Kg NO_x/tonne NH_3
Conventional	0.56 - 0.66
LCA Units	0.08

Since all hydrocarbon feed to the core plant is desulphurised there is essentially no emission of SO_2, compared with typical levels for UK based plants of around 1.5 tonnes/year/1000 tpd capacity of ammonia. With CO_2 recovered in an LCA plant there will also be a very significant reduction in CO_2 emissions to atmosphere.

There are major improvements, compared with conventional technology, in the amount of ammonia and methanol discharged in liquid effluents. Particular benefit is gained by recycling process condensate to the natural gas saturator and hence back to the reforming section. The quantity of ammonia discharged to drain is less than 25% of that discharged from an equivalent sized conventional plant; and there are similar reductions in the quantities of effluent BOD and chromate.

Reduced noise levels and visual impact provide further beneficial environmental contributions compared with conventional technology.

The LCA plant eliminates the use of the high temperature shift catalysts used in older, more conventional plant designs, and therefore eliminates the problems associated with the disposal of chrome-containing catalysts.

EFFICIENCY

Almost all conventional ammonia plants around the world produce about 5 tonnes of steam per tonne of ammonia from the process waste heat. Steam produced in the ammonia plant is used to meet the process and power requirements of the plant. A typical steam power cycle efficiency is about 25%, and to increase this the steam generation pressure and temperature have to be raised. This increased steam generation pressure, higher than that required for the process, together with the use of back pressure/passout turbine improves the overall steam power cycle efficiency of the plant.

In the LCA process the feed and fuel requirement of the process is 6.44 million kilocals/tonne compared with about 7.0 million kilocals/tonne required for modern low energy ammonia plants. This major reduction in the feed and fuel requirement of the process is achieved by the recycle of process waste heat in the GHR. The fuel saved from the process is available for use in a gas turbine combine power cycle at an efficiency of about 45% to meet the process power requirement.

Other major contributions to efficiency improvements are:

- Low steam ratio operation
- Very much reduced energy requirement for CO_2 recovery
- Much reduced inerts levels reducing the synthesis power requirements
- Reduced pressure drop through the synthesis gas generation section of the plant
- Fast start-up reducing plant start-up energy requirements

The above efficiency improvements more than outweigh the machine inefficiency due to small plant capacity and increased power requirement of the process air compressor.

CONCLUSION

The LCA concept allows a small plant to match the capital and energy efficiency of large plants and therefore opens up exciting new possibilities for the ammonia industry. ICI has demonstrated that small plants are a viable alternative for new plant investment, with the LCA plant offering reduced investment risk and short project timescale. The LCA process is part of ICI's continuing commitment to leading edge technology in ammonia.

The LCA process achieves outstanding environmental standards at no extra cost as part of the design concept.

The extra CO_2 produced makes the process ideal for the urea producer.

The inherent 12 hour start-up from cold is a design feature as is the consistently achievable low energy requirement.

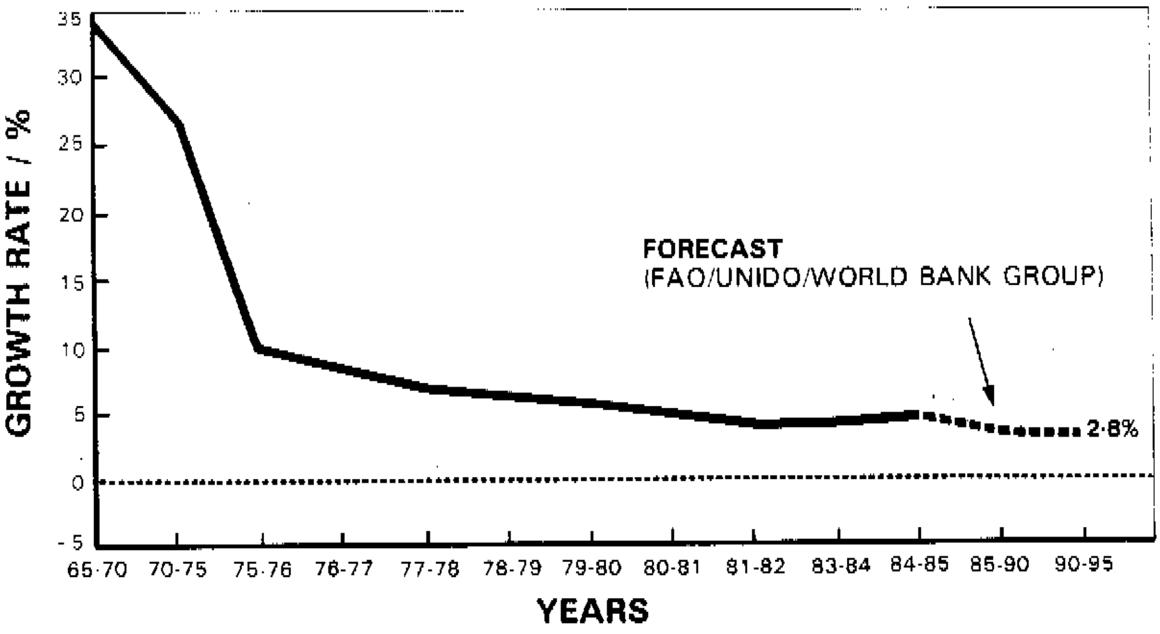
The modularisation of many essential parts of the process together with decoupling of processing steps not only simplifies on-site construction, but offers exciting options for modernisation and expansion and retrofitting of existing facilities.

The LCA concept represents the next generation of ammonia technology offering new options for the ammonia/fertiliser industry in meeting the challenges of the future.

Figure 1: World Ammonia Plants

SIZE (Tonnes/Day)	Pre-60	60-64	65-69	70-74	75-79	80-84	85-ON	TOTAL PLANTS
<200	13	11	11	12	16	6	4	73
<400	6	16	22	19	18	9	3	93
<600	4	6	21	8	7	2	5	53
<800	3	4	18	19	8	2	8	62
<1000		2	16	17	21	7	7	70
<1200		1	8	8	37	19	25	98
<1400			3	9	24	25	21	82
1400+			2	3	3	2	5	15

Figure 2: World Growth Rate of Fertilizer 'N' Consumption



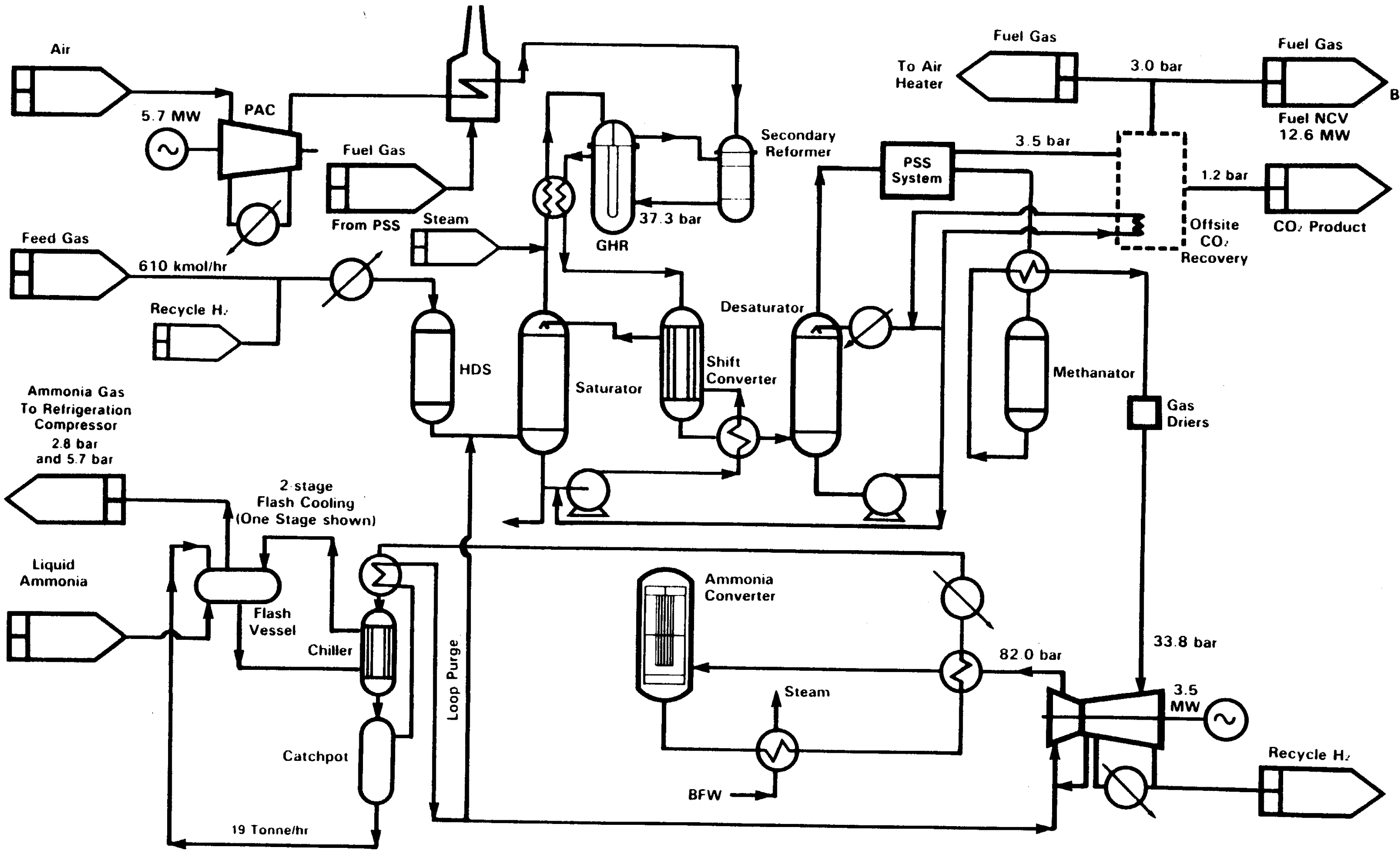


FIGURE 3. LCA PROCESS DIAGRAM

Fig. 4.

AUTOMATIC START-UP — EQUIPMENT

— Air Compressors	2
— Synthesis Gas Compressors	2
— Refrigeration Compressors	
— Turbo-Alternator	
— Fired Heaters	4
— Fired Boiler/Superheater	
— Pressure Swing Adsorption Units	2
— Cooling Water	
— Demin Water Plant	
— Syn Gas Driers	

Fig. 5.

AUTOMATIC START-UP - SEQUENCE CONTENT

EXAMPLE: COMPRESSOR:

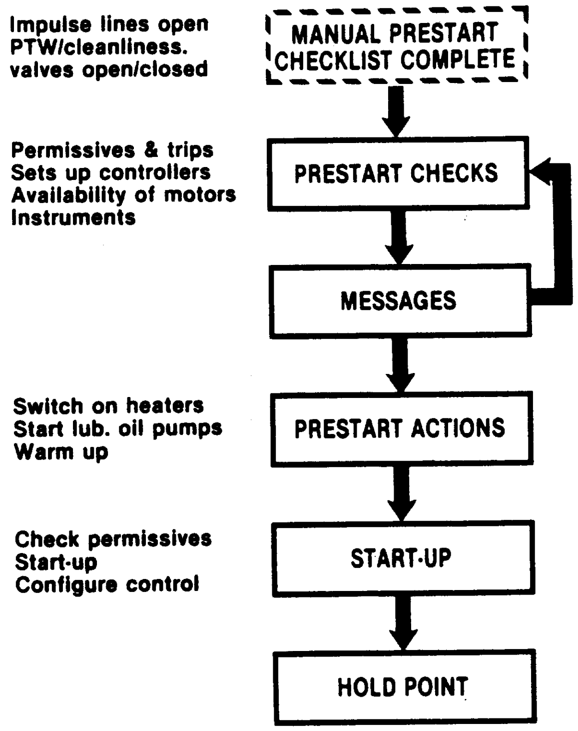
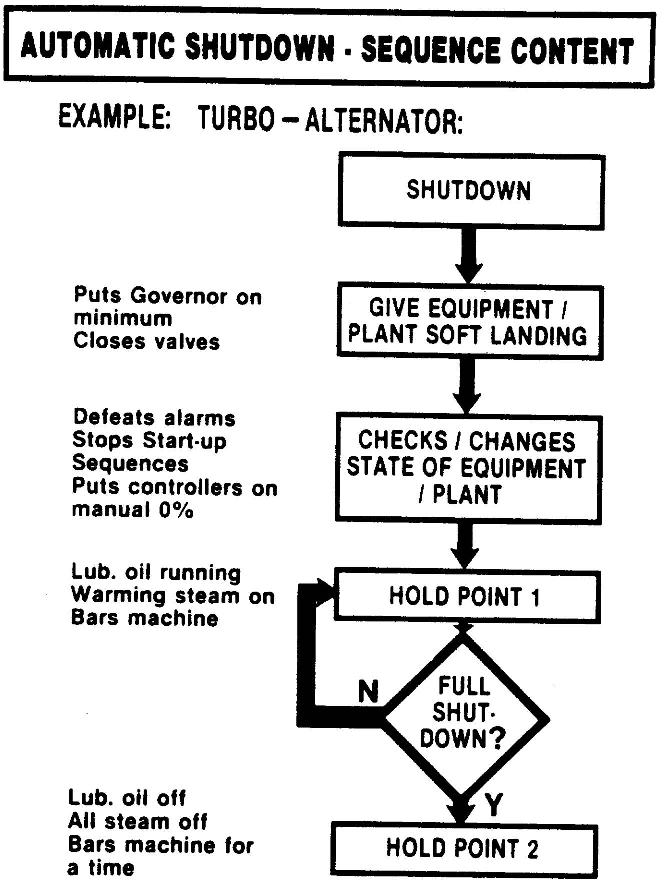


Fig. 6.


AUTOMATIC SHUTDOWN - SEQUENCE CONTENT
EXAMPLE: TURBO – ALTERNATOR:
SHUTDOWN
Puts Governor on minimum
Closes valves
GIVE EQUIPMENT / PLANT SOFT LANDING
Defeats alarms
Stops Start-up Sequences
Puts controllers on manual 0%
CHECKS / CHANGES STATE OF EQUIPMENT / PLANT
Lub. oil running
Warming steam on
Bars machine
HOLD POINT 1
N
FULL SHUT-DOWN?
Y
Lub. oil off
All steam off
Bars machine for a time
HOLD POINT 2

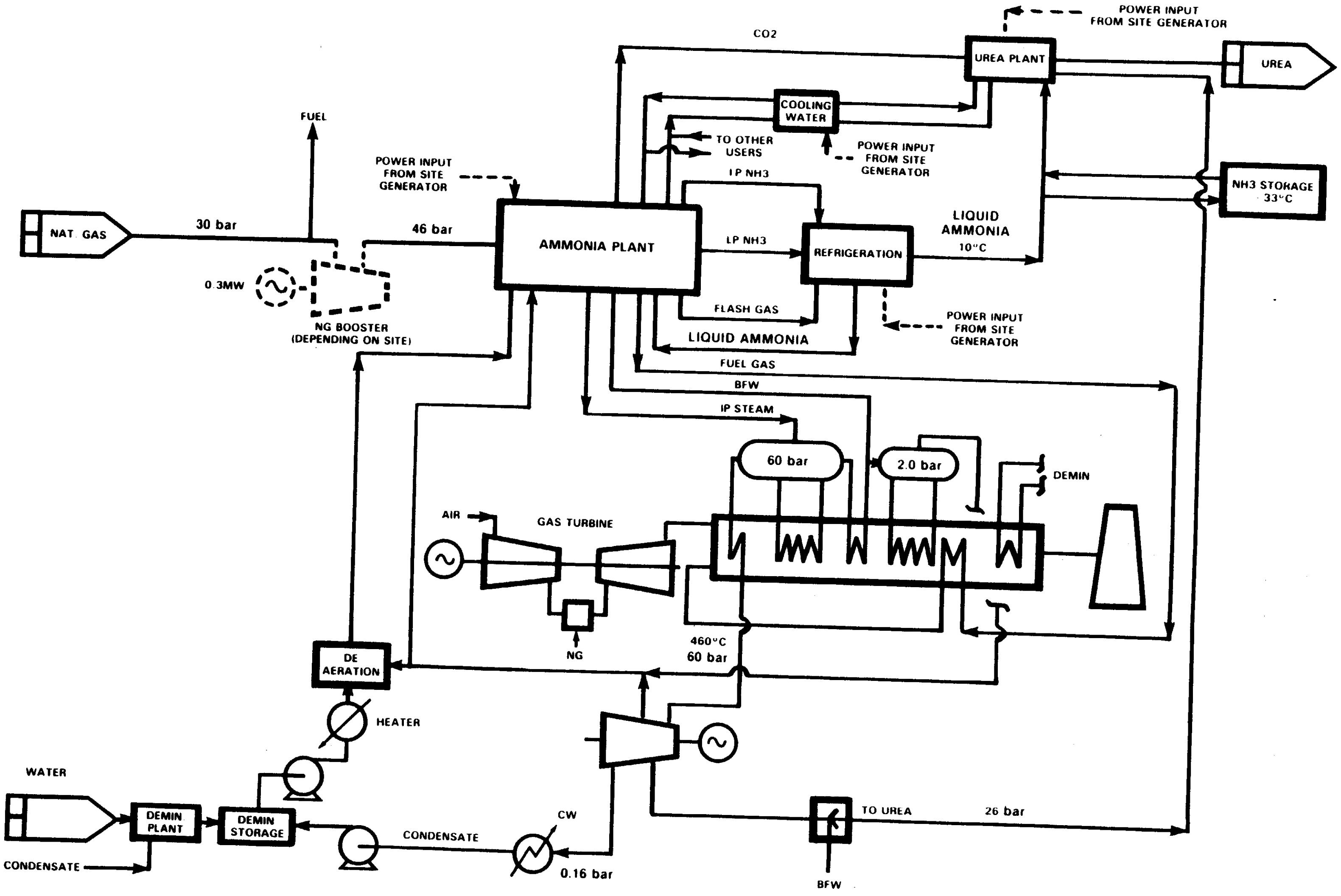


FIGURE 7. LCA/UREA INTERGRATION