Ammonia industry—today and tomorrow

Innovations in technology and best practices facilitate economic survival for global operating companies

M. P. SUKUMARAN NAIR, FACT Ltd., Cochin, Kerala, India

The ammonia industry provides nitrogenous fertilizers from hydrocarbon-based feedstocks. The first ammonia process was developed 90 years ago. Over time, technology and new equipment have improved operating costs and enabled building large plants. Yet, most ammonia facilities use natural gas (NG) as a feedstock. Likewise, the ammonia process is an energy-intensive operation. Higher energy and feedstock costs have adversely impacted the profitability of older, smaller operating facilities.

Demand for ammonia and fertilizers by developing countries increases annually. However, higher operating costs devastate the profitability of ammonia plants. Technology can be a solution to this industry. New developments are reducing operating costs and facilitating the use of other feedstock over natural gas.

TECHNOLOGY UPDATE

On the technology front, the ammonia plant flowsheet and equipment layout has endured minor changes from the original processing route developed in the 1960s. This processing method is accepted as the most efficient and economic route for ammonia production (Fig. 5). However, every processing stage and unit operation has undergone significant and considerable improvements and unique innovations. These modifications improved the operating economics, increased processing efficiencies, lowered environmental burdens, upgraded operational safety and reduced total plant/operation risks.

Feedstock sulfur removal. Feedstock NG and light hydrocarbons invariably contain small quantities of sulfur compounds, which are mostly downstream process catalysts. Consequently, these compounds are removed from the feed gas by hydrogenating it to 350–400°C. The sulfur compounds are converted into hydrogen sulfide (H_2S) in a desulfurizer, in the presence of cobalt molybdenum (CoMo) catalyst. The H_2S is adsorbed on palletized zinc oxide to form zinc sulfide. The hydrogen, normally provided by the synthesis section, and the zinc sulfide remain in the adsorption bed, which deactivates over time and must be replaced.

The desulfurization reaction is initiated by the hydrogenation step. Organic sulfur compounds are converted into H_2S and quantitatively absorbed on palletized zinc oxide:

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

This catalyst is manufactured from high-purity raw materials, essentially free of arsenic and chlorine that may poison downstream catalysts. The sulfur pickup rate is very dependent on temperature, porosity and surface area of the zinc oxide pellets. A normal service life for desulfurization catalyst is 5–7 years.

Adiabatic pre-reforming. This process eases the burden of endothermic tubular reforming. Adiabatic pre-reforming improves the efficiency of the total reforming process and eliminates many problems encountered in conventional tubular steam reformers. Pre-reformer catalyst is nickel (Ni) based on magnesium alumina spinel oxide. It is characterized by high-reforming activity, improved tolerance for sulfur and greater resistance to carbon formation at low steam-to-carbon ratios. Such catalysts are available for heavy hydrocarbon feedstock from NG to naphtha.

Tubular reforming. The desulfurized feed gas contains less than 0.1 parts per million (ppm) sulfur and is mixed with superheated process steam. This mixture is heated to 500–600°C and introduced to the primary reformer. The reformer is usually a rectangular-tubular furnace in which the feedstock-steam mixture is heated using externally fired burners. The primary reformer tubes contain Ni catalyst and are externally heated to support the endothermic reaction.

Typical reformer outlet temperatures range between 815°C and 900°C to minimize the CH_4 slip. Reformer-exit CH_4 equilibrium is favored by higher tube outlet temperature, higher steam-to-gas ratio and lower exit pressure. All have tremendous technological and economic implications. A 5.5°C rise in the tube outlet temperature can reduce the feed input by 1.3% and yield an equal increase of steam generated in the waste-heat recovery section. Metallurgical limitations of tubes, endothermic heat requirements and economics of downstream pressure operations limit choices.

Steam-to-carbon ratio—the molar ratio of steam-to-reactive carbon contained in the hydrocarbon maintained in the primary reformer—varies from 2.8 to 3.4 with NG to naphtha. A higher steam-to-carbon ratio drives the reaction closer to the equilibrium and reduces hydrocarbon slip:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H = +206.3 \text{ KJ/mol}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -41.2 \text{ KJ/mol}$$

Two important developments in the reforming technology occurred regarding catalyst and metallurgy of the reformer tubes. Both developments are driven to increase adaptability to varying feedstock slates and increased energy efficiency. *Continued*

Experienced petrochemical— ammonia

The ammonia industry is a vital key in the production of nitrogenous fertilizers. It is one of the most developed segments of the petrochemical processing industry. Ever since the invention of the Haber-Bosch process in 1913 and subsequent developments spanning over 90 years in the modern ammonia industry, fixation of atmospheric nitrogen as ammonia and its subsequent conversion to agrochemicals contribute to meet 40% of the world's protein needs. Global ammonia production in 2004 reached 141.4 million metric tons (MM metric tons), 90% of which is directly used to manufacture mineral fertilizers (Table 1). Fertilizer demand is projected to increase 1.6%/yr from 2004 to 2010, and growth is occurring in developing nations of Asia-Pacific and in Russia (Tables 1 and 2).

The ammonia industry consumes around 1.2% of the world's energy resources (Fig. 1). Over the past three decades, significant improvements in the energy efficiency, safety and environmental friendliness of ammonia production have been achieved. Thus, the specific energy consumption, waste generation, greenhouse gas (GHG) emissions and accident rate in the ammonia industry are trending downward.

Global ammonia trade has also increased significantly. Worldwide ammonia production increased by 7% in 2004; availability was in short supply in the inter-regional trade due to capacity constraints and rising maritime-freight rates. Major production centers are the Former Soviet Union (FSU) and the Middle East where natural gas supplies are abundant (Table 1). Major ammonia importers are India and the US. Nearly 62% of the 8.476 MM metric tons of ammonia exported from the Middle East is sent to India. Last year, US demand for imports increased (Table 2).

Price. The price for ammonia is highly volatile, with the lowest recorded price of $106 (CFR India) per ton in October/December 2002, and the highest as $326.27 (CFR India) in January/March 2004 (Fig. 2). The average price ranges between $117 and $304 (CFR India). In 2003, approximately 13.776 MM metric tons of liquid ammonia was traded globally.

Major exporters are the Middle East (Saudi Arabia, Bahrain and UAE), Former Soviet Union (Russia and Ukraine), Canada, Germany, The Netherlands, Indonesia and Trinidad. India, South Korea, Western Europe, Jordan, Latin America and the US imported the bulk of the ammonia produced in other countries.

Natural gas (NG), predominantly methane (CH_4) is the best feedstock for ammonia production. A recent survey shows that 71% of the world's ammonia capacity is based on NG. Other feedstock includes naphtha, LPG and refinery gases (5.6%), fuel oil and liquid residues (3.7%) and coal, coke and coke oven gas (19%). Developments for gasification suggest that coal is a potential prime feedstock for ammonia, especially due to unprecedented price increases for oil and NG.   *Continued*
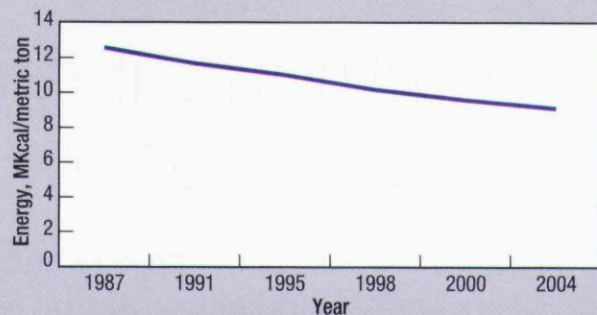
FIG. 1 Average energy consumption of ammonia facilities—1987 to 2004.
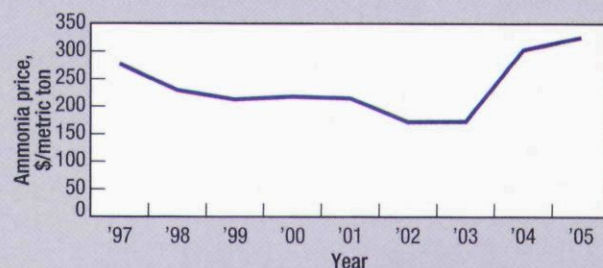
FIG. 2 Ammonia pricing from 1996 to 2005.

A very high and stable catalytic activity is needed for favorable heat transfer and lower pressure drop in the tubes. It is possible to significantly increase throughput under constant pressure drop and stable tube-wall temperatures. The carrier for the catalyst must have good mechanical strength, and the catalyst requires large surface area. Alkali-promoted catalysts prevent carbon formation in the steam reformer and minimizes hot-band formation when reforming naphtha or NG.

Developments in furnace-tube metallurgy. The reformer tubes, which are usually designed to limit creep-rupture life to 100,000 hours, operate under severe conditions of an oxidizing environment. These processing conditions include a very hot atmosphere containing corrosive oxides of sulfur, nitrogen and particulates. The tube material is also under strain of carburization and metal dusting, and is subjected to extensive cyclic thermal and pressure shock loadings. Thus, the tube construction materials must have proven mechanical strength, high-temperature corrosion resistance and amenability to casting and welding. Moreover, they must be easily available at affordable costs.

The new alloys, such as HK 40 and a wide variety of modern super alloys, are possible construction materials for furnace tubes. Cast alloys are the prime choice; they tolerate significantly higher concentrations of carbon, silicon, tungsten, molybdenum, etc., which are added to enhance mechanical properties and increase corrosion resistance. Within the modern ammonia processing, the metal working of the cast tubes has become more difficult.

Another elevated-temperature degradation process for austenitic stainless steels is sensitization caused by precipitating chromium carbides preferentially at grain boundaries. It may occur during fabrication from the heat of welding, improper heat treatment or through service exposure.
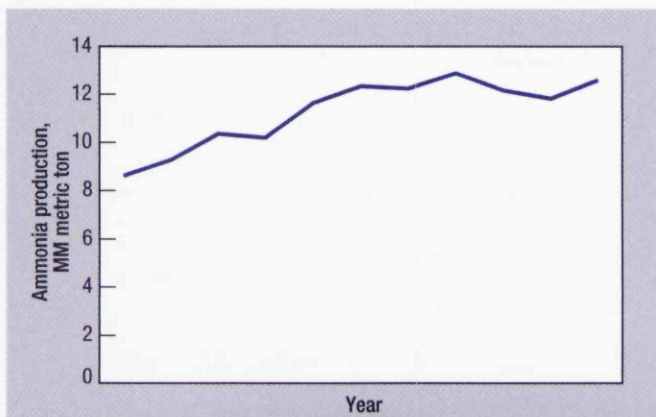
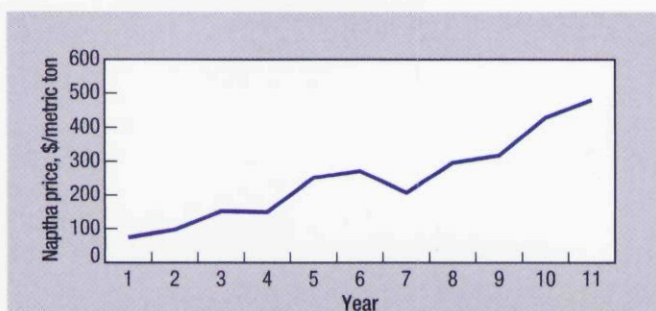**FIG. 3**   India's ammonia production from 1993 to 2004.

FIG. 4   Naphtha pricing from 1995 to 2005.

Tube failures in primary reformers are attributed to creep rupture, stress rupture, bowing or hot bands. Common failure causes of reformer tubes include: over firing, thermal shocks, steam condensation over the catalyst, and impact of thermal and pressure cycling from frequent startups and shutdowns. Hence, monitoring the health of the tube is a vital aspect of reformer operations. Regular assessment of the tube-wall temperature, maintaining a well-defined burner flame geometry and ensuring even flow through the tubes can achieve a better service life for the tube. The physical condition of the tubes should be assessed during annual turnarounds through nondestructive testing (NDT) methods; for creep detection, monitoring methods include eddy current, ultrasonic or laser profilometry methods.

Presently, the economic choice of tube metallurgy is based on life cycle costs. Several reformers are revamped using improved metallurgy of the tube material with increased creep-rupture strength and improved carburization resistance and drastically reduced plant outage. It has been well-established that it is more cost-effective to specify a material that will provide an extended life for areas that are difficult to repair—or in components that would cause major shutdowns due to failure, such as the primary reformer tubes. In these situations, the original cost of the material is insignificant compared to the lost production resulting from the component failure.

The gas-heated reformer or the tandem reformer replaces the tubular reformer with a heat exchanger applying tubes filled with the reforming catalyst. Effluents from the secondary reformer provide

NG is also traded around globally in the form of liquefied natural gas (LNG) and piped through cross-country pipelines. Major exporters of LNG are located in the Middle East, Russia, Southeast Asia, Australia, Algeria, Nigeria, Canada and Mexico. Major LNG importers include Japan, European Union, US, South Korea and Taiwan. Most long-distance NG pipelines are located in Europe and North America.

NG enjoyed a price advantage over other feedstocks for a long time due to restricted availability at close proximity to oil fields, huge investments needed for liquefaction, transport of the cryogenic liquid, re-gasification and pipeline infrastructure at the consumer's end. This situation has slowly changed as increasing demand for NG has facilitated the construction of LNG terminals in different countries.

Compressed natural gas (CNG) is slowly emerging as a low-cost feedstock for ammonia plants. The technology for CNG capture, transport and delivery is proven. In addition, investments to capture and compress NG from stranded gas fields are lower than for LNG terminals.

Transport of CNG is simple and easy to implement. Shipping CNG is cheaper than LNG for distances up to 3,500 km. At greater distances, the shipping costs for CNG exceed LNG expenses, thus making LNG more attractive as the transport media—more gas (three times the volume of gas) per shipment. With the ensured availability of CNG, coastal ammonia plants based on naphtha or fuel oil may find it feasible to change feedstocks to regain financial viability.

INDIA

The Indian ammonia industry has an installed annual capacity of 12.8 MM metric tons, and the production during 2003–04 was 12.53 MM metric tons (Fig. 3). Nearly 61% of the ammonia produced in India is based on NG. Of the 38 plants, 35 are now operating and three are closed due to lack of viability under the new fertilizer pricing policy. Fifteen plants operate in the private sector, 14 in the public sector and six in the cooperative sector. Besides a domestic production of 12.595 MM metric tons, India imported around 1.33 MM metric tons of ammonia during 2003–04 (Table 2).

Supply and balance. International Fertilizer Industry Association (IFA), based in Paris, estimated that the global nitrogen supply and demand balance will remain tight in the short term but will expand into a surplus situation in subsequent years. In terms of cumulative demand over supply (total capability of ammonia), the growth in supply is forecast at 2.5%/y compared with an annual growth in demand of 1.5%. A surplus is expected to emerge by 2006 and to increase substantially by 2009, assuming that all announced capacity projects are completed in time. However, the growth rate of this surplus will start to decelerate by the end of the decade.

Between 2005 to 2009, new projects and expansions will add about 24 MM metric tons of urea capacity, of which 60% will be located in consuming countries. In terms of regional

distribution, West Asia will contribute close to half of the new capacity additions during this period, followed by China with a 35% contribution and the remaining 15% will come mostly from Russia and India.

The higher cost of NG prevailing in North America, Western and Central Europe, Northeast Asia and India provide no incentives for investments in modern, large and cost-competitive capacity in the region. Instead, gas-rich regions of West Asia, Russia and the Caribbean continue to provide strong business perspectives for sustained investments. In addition, several plants remain idle in the US and India due to high feedstock cost for gas or liquid.

Due to recent hikes in crude oil pricing, feedstock prices for ammonia production—NG and naphtha—have increased considerably. In India, the prevailing NG price along the HBJ pipeline is $3–4.5 per MMBtu, whereas that of fuel oil is $11 per MMBtu and for naphtha in the range of $14–15 per MMBtu (Fig. 4). Increasing liquid feedstock prices have put tremendous pressure on naphtha- and fuel oil-based plants in India. Some plants are closed; others operate while incurring heavy losses.

China and India, major importers of urea until the late 1990s, developed indigenous production capabilities and stopped imports. China began exporting 1 MM metric tons of urea by 2001. Global capacity buildup curtailed due to loss of export markets to India and China. The situation is slowly changing, and imports to India, restated in 2003, may increase due to the likely closure of nearly 3 MM metric tons of urea capacity following the changes in the fertilizer pricing policy.

China does not have proven NG sources or easy access to LNG. However, it is the largest coal producer in the world. Hence, China continues its ammonia expansion program by planning 10 coal-based plants to produce 3.7 MM metric tpy of ammonia. In contrast, two major Indian coal-based ammonia plants, which contributed significant expertise to coal gasification technology, were shut down due to cost. From the international scenario, technology will play a pivotal role that will ensure the growing needs of fertilizers.

Other feedstocks for ammonia manufacture include light hydrocarbons such as liquefied petroleum gas (LPG), fuel oil, refinery residues and coal. These feedstocks have yet to be proven for technical and commercial viability in modern large-capacity plants.

Current trend. The ammonia industry is constructing higher-capacity single-stream plants. Single-stream plants with capacities ranging between 2,500 metric tpd and 3,000 metric tpd are operational. Capacities up to 5,000 tpd are being planned by major technology suppliers. This achievement is possible through the continuous efforts to optimize and improve ammonia synthesis technology. The benefits for larger units include the advantages from economy-of-scale. Doubling the size of a single-train unit can potentially reduce the capital-related production costs by 20%. **HP**
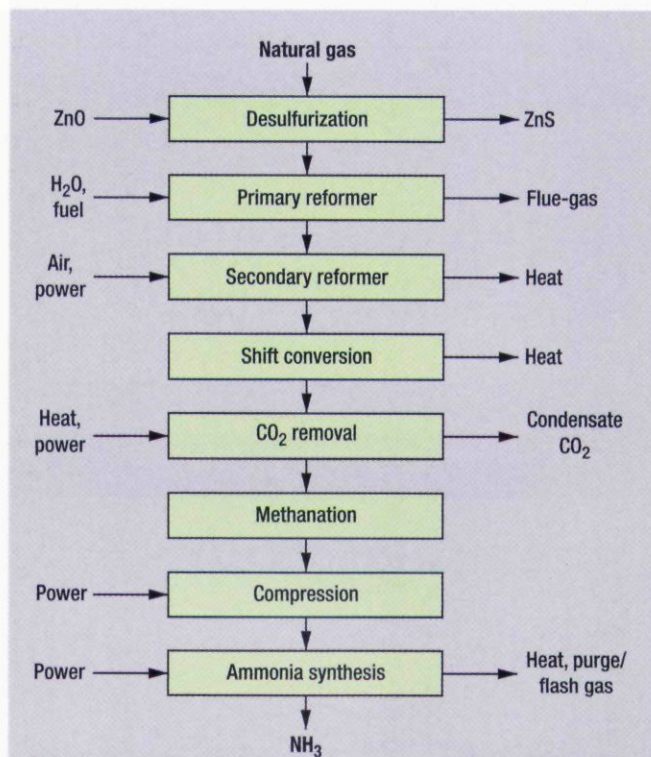

FIG. 5   Ammonia process flow sheet using natural gas reforming.

the heat energy for the reforming reaction. Although this method has several advantages over the conventional tubular reformer, it is yet to gain acceptance in modern large-capacity plants.

Flue gas leaving the radiant box has a temperature of 1,100°C. Only 50–60% of the heat supplied is directly used within the process. The remaining enthalpy from the flue gas is recovered in the flue-gas heat-recovery train to pre-heat the incoming feedstock, generate steam, superheat steam and for other process requirements. The flue gas leaves the convection section and is vented to atmosphere at 100–200°C, which is the main emission source from the plant. It contains mainly carbon dioxide (CO_2) and small amounts of nitrogen oxides (NO_x), carbon monoxide (CO) and sulfur dioxide (SO_2).

Secondary reforming. Secondary reforming is partial oxidation of residual CH_4 from the primary reformer. Hot process air is added through a specially designed burner into the reactor, in which internal combustion occurs. The extent of primary reforming is adjusted so that the air supplied to the secondary reformer meets the heat balance and stoichiometric synthesis gas requirement. The gas/air mixture is then passed over a Ni-containing catalyst where the reforming reaction proceeds to near completion:

$$2CH_4 + O_2 \ (+4N_2) \rightarrow 2CO + 4H_2O \ (+4N_2)$$
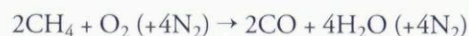
$$\Delta H = -71.4 \ KJ/mol$$

The secondary reforming catalyst is nickel oxide on alumina support and has a high thermal resistance and stable activity. Exit gases exit from the secondary reformer at 950–1,000°C with most

TABLE 1. World ammonia situation—2003

Production		Major exports		Major imports	
Country	MM metric ton	Country	MM metric ton	Country	MM metric ton
China	30.207	Russia	2.4999	US	5.415
India	12.595	Trinidad	3.251	India	1.085
US	8.768	Ukraine	1.467	South Korea	0.841
Russia	9.113	Indonesia	1.257	France	0.609
Ukraine	3.934	Canada	0.674	Belgium	0.477
Canada	3.646	Qatar	0.349		
Trinidad	3.574	Saudi Arabia	0.372		
Indonesia	4.254	The Netherlands	0.476		
Others	32.70	Others	3.431	Others	5.35
World total	108.79	World	13.777	World	13.777

of the hydrocarbon in the feed converted to CO, CO_2 and hydrogen (H_2) together with added nitrogen. The process gas is cooled to 350–400°C in a process heat-recovery steam boiler or boiler feedwater heater.

CO conversion. The cooled reformed gas contains 12–15% CO, with the balance as H_2, nitrogen (N_2), CO_2 and small amounts of argon and CH_4 (dry basis). Most of the CO is converted to CO_2 by passing the process gas through a bed of iron oxide/chromium oxide catalyst at 370–400°C in a high-temperature converter and then over a copper oxide/zinc oxide catalyst at about 200–220°C in a low-temperature converter. The residual CO content of the gas is 0.2–0.4%:

$$CO + H_2O \rightarrow CO_2 + H_2$$

$$\Delta H = -41.2 \text{ KJ/mol}$$
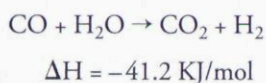
Now, the gas contains mainly H_2, N_2, CO_2 and excess process steam that was supplied at the primary reforming stage. Most of the steam is condensed by cooling the gas before it enters the CO_2-removal system. The condensate normally contains 1,500–2,000 ppm ammonia and 800–1,200 ppm methanol (CH_3OH), as well as some CO_2 and catalyst dust, etc. In older plants, the process condensate is stripped in a column in which low-pressure (LP) steam is at the bottom. A mixture of steam and gases is vented to the atmosphere, while the stripped condensate after polishing is used as boiler feedwater.

Medium-temperature shift (MTS) catalysts now replace standard high-temperature shift (HTS) catalysts in ammonia and hydrogen plants operating at very low steam-to-carbon ratios. Most low-temperature shift (LTS) catalysts in the market have high resistance

TABLE 2. Indian ammonia imports—2003–04

Country	MM metric ton
Qatar	0.328
Saudi Arabia	0.226
Iran	0.116
Bangladesh	0.151
UAE	0.094
Others	0.411
Total	1.326

to water and chlorine poisoning. Recently, the methanol byproduct formation across LTS catalysts has become an environmental issue. New-generation LTS catalysts are capable of reducing methanol formation. A new development in the HTS-shift converter is a specially designed boiler embedded in the catalyst beds for in situ heat removal; thus, the reactor is very efficient.

CO₂ removal. The economics of hydrogen and ammonia manufacturing plants heavily depend on the efficiency and reliability of CO_2-removal systems. Over the last 30 years of technology development, several innovations for this processing step have increased absorption efficiency, reduced CO_2 slip to ppmv, reduced energy requirements to regenerate CO_2, effectively reduce corrosion of plant equipment, emergence of nontoxic and environmentally friendly solvent systems and activators for absorption, a shift from physical and chemical modes for absorption to a combination of both, improvements in mass transfer through better gas-liquid contact, and so on.

The converted gas usually contains 18–22% CO_2, which is removed by chemical or physical absorption process. The solvents
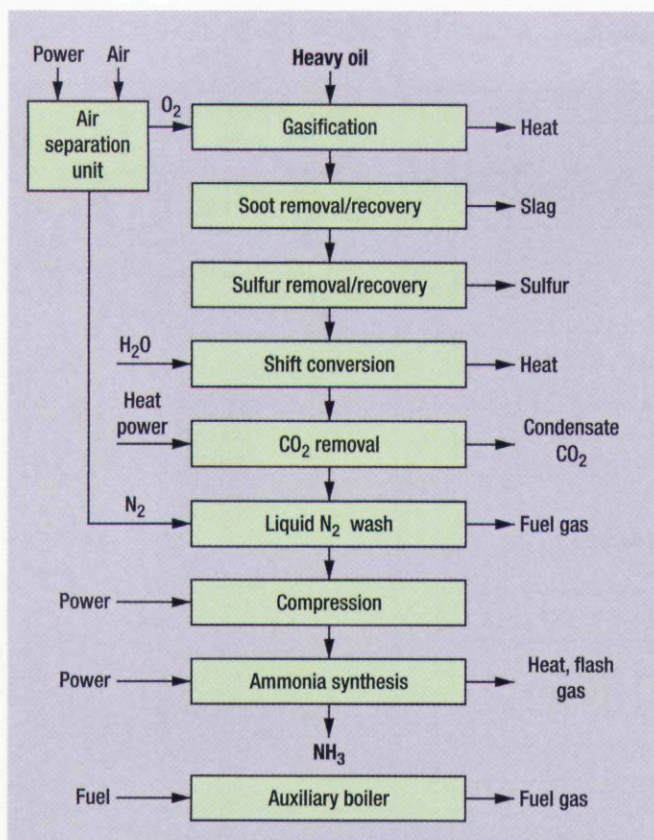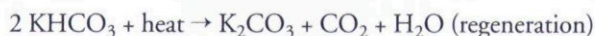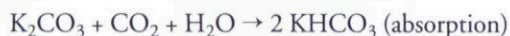
FIG. 6 Ammonia process flow sheet using heavy fuel with partial oxidation methods.

used in chemical processes are mainly aqueous amine solutions or hot-potassium carbonate solutions. For physical absorption, solvents such as glycol dimethyl ethers and propylene carbonate are used.
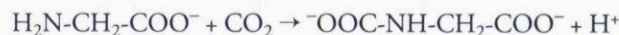
Vanadium pentoxide, arsenic trioxide, piperazine and other compounds depending on the process are used as promoters or catalysts. In the amine processes, CO_2 absorption occurs by forming amine adducts that are heat sensitive and regenerated by heating the solution. In the physical absorption process, CO_2 is dissolved under pressure in methanol without combining in a chemical sense. Regeneration is achieved by simple flashing of the solution. Pressure swing absorption (PSA) is used for CO_2 removal in smaller plants.

Apart from the solution for absorption and its characteristics, tower design, internal packing, solution distributors and redistributors, solution flowrates, etc., are also important. Currently, proven designs are available from proprietary suppliers, in addition to technical backup for commissioning and troubleshooting. Thus, selecting the best CO_2 option is easier.
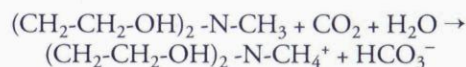
Hot-potassium carbonate process. This process is activated by 3% diethanolamine (DEA). The solution is inhibited by vanadium pentoxide (V_2O_5) to reduce the corrosion impact. Usually, the solution composition is 30% potassium carbonate plus 0.3–1% activator and the corrosion inhibitor. Improved amine activators with more stability and are less prone to degradation are being developed:

$$K_2CO_3 + CO_2 + H_2O \rightarrow 2\,KHCO_3 \text{ (absorption)}$$

$$2\,KHCO_3 + heat \rightarrow K_2CO_3 + CO_2 + H_2O \text{ (regeneration)}$$

Glycine process. This process uses an aqueous solution mix of potassium carbonate, amino acetic acid (glycine) and DEA. The carbonate content is usually 29 wt% and the activators are less than 2%. The solution constituents are nontoxic. A two-stage absorption involving semi-lean (feed at the middle of absorber) and lean (top) solution is used. The semi-lean flow is not cooled to increase the kinetics for absorption. Conversely, the lean flow is cooled to enhance the approach to equilibrium and minimize CO_2 slip:

$$H_2N\text{-}CH_2\text{-}COO^- + CO_2 \rightarrow {}^-OOC\text{-}NH\text{-}CH_2\text{-}COO^- + H^+$$

$${}^-OOC\text{-}NH\text{-}CH_2\text{-}COO^- + H_2O = H_2N\text{-}CH_2\text{-}COO^- + HCO_3^-$$

Methyl diethanolamine process. Currently, methyl diethanolamine (MDEA) process is extensively used in ammonia plants for bulk CO_2-removal. Several units are operating efficiently globally. MDEA process has revolutionized technology CO_2-removal in terms of process economics, reliability, energy consumption and corrosion control. The solution consists of MDEA (a tertiary amine), piperazine (a cyclic amine as activator) and water; it is less basic in nature compared to glycine or DEA. CO_2 absorption by pure MDEA is quite low but is enhanced by activators, and a variation in the activator concentration allows shifting thermodynamic behavior from more physical to more chemical nature:

$$(CH_2\text{-}CH_2\text{-}OH)_2\text{ -}N\text{-}CH_3 + CO_2 + H_2O \rightarrow$$
$$(CH_2\text{-}CH_2\text{-}OH)_2\text{ -}N\text{-}CH_4^+ + HCO_3^-$$

For the urea plant associated with an NG-based ammonia plant, a major constraint is that CO_2 generated from the front end of the ammonia plant does not meet the requisite demand for urea production. Several plants have installed CO_2 recovery units from primary reformer flue-gas streams. This has lowered GHG emissions from the facility.

In the 1990s, the gas-heated reformer (GHR) process replaced the conventional tubular reformer and uses PSA for CO_2 removal from the process gas stream. However, for large-capacity ammonia plants, PSA has not yet become proven economically.

Methanation. Gas from the absorber after CO_2 removal contain only small amounts of CO and CO_2 that must be removed; it is a poison to ammonia synthesis catalyst. In the methanation reaction, CO and CO_2 are converted to CH_4 and water by passing the absorber gas through a reactor containing Ni catalyst at 350°C. The development of efficient shift catalysts and CO_2 removal systems reduced operating temperature for the methanation catalyst:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad \Delta H = -206 \text{ KJ/mol}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \Delta H = -165 \text{ KJ/mol}$$

The CH_4 is an inert gas in the synthesis reaction, and formed water is removed by cooling and condensing it. The gas, after methanation and cooling, contains H_2 and N in the stoichiometric ratio of 3:1 and is called synthesis gas.

Ammonia synthesis. Converter technology and synthesis catalyst have been combined to achieve higher energy efficiency within the synthesis section. Catalysts play a vital role in this

development. Most plants have installed pre-reduced catalyst to minimize startup time.

Synthesis gas is compressed to 100–200 bars using centrifugal compressors, usually driven by high-pressure (HP) steam turbines. The reaction uses an iron catalyst at 350–550°C. Ammonia formation reaction is exothermic; thus, generated heat is used for process steam production. Only 20–30% of the synthesis gas is converted with each pass through the converter; thus, a recycling loop is required to separate ammonia from the converter effluent and for admitting fresh makeup gas. During this operation, inert gases, contained in the synthesis gas (argon, methane, etc.), build up in the synthesis loop and are maintained by a continuous purge of 10–15%. The purge gas is cooled to separate NH_3, scrubbed with water to remove remaining ammonia, and used as fuel in the reformer or sent for hydrogen recovery.

Condensing product ammonia is achieved by a refrigeration system, and product ammonia is sent to the storage. The liquefied product ammonia is either used directly in downstream plants or stored in tanks. These tanks are usually fully refrigerated with capacities ranging between 10,000 to 50,000 metric ton, pressurized spheres (3,000 metric ton) and bullets (20 metric ton)

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad \Delta H = -91.8 \text{ KJ/mol}$$

The ammonia reaction equilibrium is favored by low temperature and high pressure. Catalyzed reaction rates are increased by higher temperatures and pressure. **Result:** Most ammonia synthesis loops use converters with multiple beds with inter-bed cooling.

A breakthrough in ammonia synthesis technology is the development of ruthenium metal-based catalyst on a proprietary graphitic structure. It has an intrinsic activity up to 20 times higher than the conventional iron-based catalyst. This catalyst can maintain higher activity at low temperature and pressure, and operates over a wide range of H_2/N_2 ratios.

Another development in ammonia-catalyst technology is the granular wustite (non-stoichiometric ferrous oxide) catalyst with promoters as Ca, aluminum, potassium, and rare-earth elements with higher activity at low temperature and pressure, faster reduction rates and increased mechanical strength and resistance to poisons.

Modern ammonia converters are designed on the radial-flow concept, which has inherently low pressure drop, high conversion per pass, heat removal between catalyst beds and enable using smaller sized catalyst. Thus, the recirculation rate and loop pressure drop remain low, reducing power requirements for compression. Most older plants are retrofitted with the new converter baskets to save energy and reduce strain on loop equipment.

The ammonia purge gas recovery (PGR) system recovers considerable volumes of H_2 that are otherwise lost as fuel to the furnace. Designs based on both cryogenic technology and hollow-fiber membranes have been successful. The former is more efficient in recovering H_2 from the purge, and the latter requires a lower capital investment.

Partial oxidation of hydrocarbon or coal. Partial oxidation processes using heavy fuel oil, vacuum residue from petroleum refining or coal offer an alternative route for ammonia production. Process economics and investment depend on the availability, cost and quality of feedstocks and oxygen. Other factors include environmental issues as disposal and treatment of process byproducts and wastewater.

If the feedstock is heavy fuel oil with high-sulfur content or coal, non-catalytic partial oxidation, at 50 bar pressure and 1,400°C, is applied for gasification (Fig. 6). Steam is added to the gasifier to moderate the gasification temperature. A cryogenic air-separation unit supplies oxygen and nitrogen to the process.

Reacting hydrocarbons with oxygen in the gasifier produces CO and H_2, as well as some CO_2, CH_4 and soot. Heat is recovered from the hot and dusty gases in a specially designed boiler. Soot from the process gas is removed by scrubbing it with water and separated as a carbon slurry. Sulfur compounds in the feed are converted to H_2S and separated from the process gas, using a selective absorption agent (which could be the same as in the CO_2 removal). Regenerated H_2S is then converted to elemental sulfur by the Claus sulfur recovery process.

CO is then converted to CO_2 by the water-shift reaction upon passing through two iron-catalyst beds with intermediate cooling. The CO_2 is removed by an absorption agent as in the reforming route. The residual traces of CO and CO_2 are removed in the final gas purification by a liquid nitrogen wash. Pure synthesis gas is generated; more N_2 is added to provide the stoichiometric H_2/N_2 ratio for ammonia production. The produced synthesis gas contains only H_2 and N_2—no inerts. Consequently, no purge for the ammonia synthesis loop is needed. **Result:** Loop efficiency is better than the steam-reforming process.

Coal. In coal gasification, the main stages are coal grinding, slurry preparation and slurry pulverization, in addition to those required for the heavy fuel-oil processing. Higher initial investment is needed. Higher energy consumption renders coal gasification as unviable. Still, efforts are underway to overcome these disadvantages and capitalize on mega capacities; both are partially driven by higher pricing for crude oil.

Co-production of ammonia. Gasification of residues from refining operations is well-proven and established; several installations, located in different countries, exist. This process involves non-catalytic partial oxidation of feedstocks with oxygen from an associated air-separation process to produce synthesis gas—a mixture of CO, H_2 and smaller quantities of CO_2, H_2S, soot, etc. Hot gases from the gasifier are cooled and cogenerate process steam by quenching it with water to remove dust and particulate matter. Hydrogen sulfide is separated by MEA or glycol wash.

The recovered H_2S and carbonyl sulfides (COS) are sent to the Claus reaction; sulfur is recovered in the elemental form, which can be used for sulfuric acid or fertilizer production. The entire sulfur in the residue is fixed as plant nutrient.

Synthesis gas generated from the process is similar to that from other partial oxidation processes using furnace oil (FO) or low-sulfur heavy stock (LSHS). Besides ammonia synthesis, it can also be used for methanol manufacture or power generation in the integrated gasification and combined cycle mode (Fig. 7). For ammonia synthesis, the CO in the gas is converted to CO_2 and is stripped off. Produced H_2 is mixed with N_2 from air separation in a wash column to the specification for the ammonia synthesis gas. The refinery hydrogen requirement
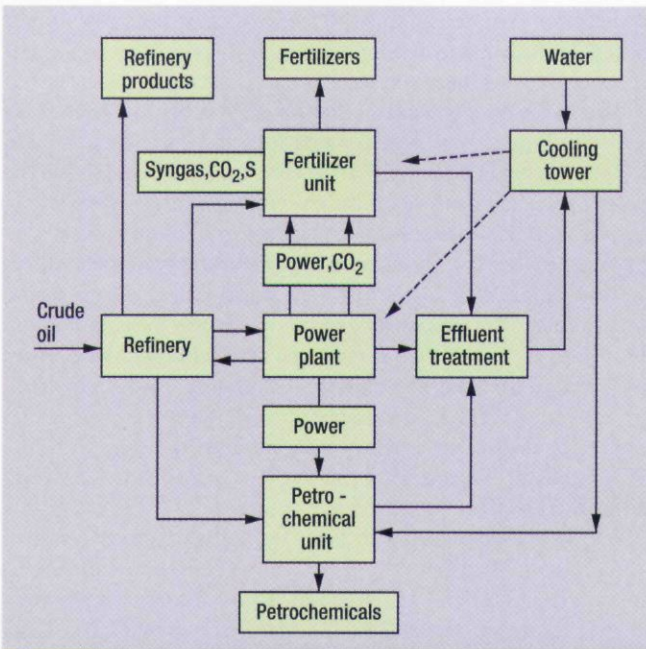
FIG. 7 Integrated chemical complex refinery fertilizer-power and petrochemicals combined operation.

for desulfurization and fuel gradation can also be met from the synthesis gas through PSA.

Environment. The environmental benefits associated with the combined operation are improved carbon recycle, total sulfur recovery and reduced CO_2 emissions. Gasification technology benefits include better disposal of heavy refinery residues, improved feedstock flexibility, higher degree of operability and reliability, and improved efficiency for synthesis gasmake. The economic are attractive due to higher system optimization and greater reductions on input costs at every stage.

For developing countries, such as China and India, industrial and agricultural consumption and total economic growth are increasing. These nations rely on imports for feedstocks and fuel requirements to support refineries and downstream facilities such as fertilizer, power and petrochemical industry. Refinery, fertilizer, power and petrochemicals are major investments and high-technology decisions. Often, these units are managed by different agencies and function as independent companies. Technology can be used to exploit the synergy between these units; it can play a major role in improving the profitability of all of these units in varying degrees.

Plant reliability. Improved plant reliability is a wholistic effect. It involves better operation and conditioning of critical equipment such as reformers, boilers, converters, compressors, and unit operations including CO_2 removal, purge-gas recovery and applying better with increased activity and service life. Startup time has been lowered over time, and the techniques for accelerated startups have been possible with pre-reduced catalysts.

The modern ammonia plant has registered a high degree of versatility with regard to onstream days. Over the years, annual turnarounds are planned in order to replace spent catalysts. Turnarounds are also planned to accommodate statutory inspections for the boiler equipment and other vital tasks that can only

be done when the unit is shut down. Some plants have adopted a strategy to plan 30 days for yearly repairs and maintenance on a two-year continued operation cycle.

Process control issues. Most plants are on distributed control system (DCS) based instrumentation. Thus, the discrete analysis of past data and understanding the behavioral trends of equipment is easy. Real-time process data reconciliation and validation assist operators to accurately model equipment and reactors. Such operator-friendly programs for online performance monitoring are available at affordable costs.

Several Indian plants have been successful in taking advantage of most reliability improvement tools. An expert group, enquiring into the efficiency levels for ammonia and urea plants of the three largest global producers, shows that energy consumption of Indian gas-based plants is better than similar plants operated in the US and China. In the case for naphtha-based plants, energy consumption figures are nearly equal on a comparable basis.

Safety, security and environmental status. Remarkable achievements have been made in the operational safety of ammonia plants. In addition, the harsh operating environment of these facilities has been reduced considerably. For example, the ammonia synthesis pressure was 350 atmospheres in the early 1960s; currently, it has been reduced below 100 atmospheres with the assistance of increased activity catalysis, better system configuration and installing more reliable equipment and process control instruments.

Every effort is made so that all sections of the ammonia plants are designed and built adhering to the inherent safety concepts. Once the plant is designed, a thorough Hazard and Operability (HAZOP) check is done at the design freeze stage and after construction. Later, the collected information is used to conduct a thorough risk analysis. Adequate provisions are made to ensure that risks to the plant, employees and local community are minimized and are within the acceptable limits. Inclusive emergency management plans are also developed and frequently tested through mock drills replicating the probable worst-case scenarios. In many plants, there are specific systems and guidelines intended to manage abnormal situations.

Several accidents have occurred in this industry, and more important, several lessons were learned from such incidents. Every accident was investigated and discussed at various international forums. From these actions, remedial measures to prevent repetition of such occurrences have been incorporated in the subsequent designs or changes in operation and maintenance philosophies were developed. In addition, the meritorious contributions by the Safety in Ammonia Plants and Related Facilities Symposium, organized annually by the American Institute of Chemical Engineers, have been instrumental in driving changes in plant design and operations.

Environmental issues. The environment management facilities ensure that plant emissions, effluents and solid wastes are properly treated and disposed. Another environmental concern is *noise*. Sources within the ammonia plant are from the reformer furnace, blowers, air coolers, pumps, compressors and PSA units. Using low-noise burners, enclosing rotating equipment, installing noise attenuation insulation for air ducting, etc., are some ways to lower noise within the plants.

Management of hazardous waste materials has become a major concern due to environmental issues. Major hazardous wastes generated from ammonia manufacturing operations are primarily byproducts and/or spent catalysts consisting of nickel, molybdenum, zinc, copper, vanadium, chromium, palladium, platinum, rhodium, etc. Other wastes include spent carbon from purification operations, and arsenic- and vanadium-bearing residues from CO_2-removal operations. In ammonia plants, waste byproducts that require special disposal procedures are chromium-bearing sludges from cooling water treatment, chemical sludge from reactors, effluent and waste-water treatment plant, waste oil from equipment, workshops and electrical installations, etc. There are earnest efforts from industry to voluntarily undertake safe disposal of such waste materials in specially designed treatment, storage and disposal facilities.

Plant security is also a prime interest issue due to threats from worldwide terrorism. There is a growing need for more detailed security guidelines to be adopted. These guidelines may be issued by professional industrial organizations or by federal government agencies.

Management outlook has also undergone a paradigm shift. Lessons learned from past failures, systematically investigating all failures for systems and equipment, practicing risk-based inspection procedures and adopting reliability-centered maintenance techniques are some of the methods now practiced as standard operating policies. On the operator's side, online performance monitoring is also a commonly adopted practice for streamlining plant performance against the targets. Predictive trouble shooting and preventive

maintenance of equipment have been very successful in reducing plant outages.

Based on the operating experience and research, common problems encountered in plants are addressed to achieve a reliable, efficient and sustainable operation. These efforts identify best operating practices, explore retrofit options available and suggest management methods for abnormal situations, and, thus, achieve total plant optimization. The driving force of production and innovation within the ammonia industry is to become energy efficient, demonstrate environmental quality and yield economic/ profitable operations in the global markets. **HP**

Dr. M. P. Sukumaran Nair is the chief superintendent production at the Cochin Division facilities of The Fertilizers and Chemicals Travancore (FACT) Ltd., India's pioneer fertilizer and chemical manufacturing and engineering consultancy organization. He was the managing director of the state-owned chlor alkali major, Travancore Cochin Chemicals Ltd., Cochin. He holds BS degrees in chemistry and chemical engineering and a postgraduate degree in ecology and environment. Dr. Nair also holds an MBA and a doctorate in environmental management. He joined FACT in 1971 and is well-experienced in process plant design and operation, troubleshooting and management in the HPI. Dr. Nair is a fellow of the Institution of Engineers (India), was the chairman of the Institution of Engineers (India), Cochin, and a member of the AIChE. He is also a member of several expert advisory committees to the central and state governments and has published over 50 papers. He is listed in the *Marquis, Who's Who in the World* and by the International Biographical Centre, Cambridge, England, and can be reached by e-mail: mpsn@vsnl.com.