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FINAL REPORT

STEAM METHANE REFORMING IN MOLTEN CARBONATE SALT

Department of Energy ERIP Grant No. DE FG01-91CE15404

May 1996

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1. EXECUTIVE SUMMARY

This report documents the work accomplished on the project "Steam Methane Reforming in Molten Carbonate Salt."

This work was financed by DOE Grant DE FG01-91CE15404 under the Energy Related Inventions Program. The invention was submitted to NIST and received a favorable recommendation (ERIP Recommendation 404).

Contractual effort commenced on September 16, 1991, and continued until all contract funds were expended. As explained below, work is continuing on a particularly promising aspect of this technology under internal funding.

This effort has established the conceptual basis for molten carbonate-based steam reforming of methane. It has not proceeded to prototype verification, because corrosion concerns have led to reluctance on the part of large hydrogen producers to adopt the technology. Therefore the focus was shifted to a less corrosive embodiment of the same technology. After considerable development effort there, it was discovered that a European company (Catalysts and Chemicals Europe) was developing a similar process ("Regate"). Accordingly the focus was shifted a second time, to develop an improvement which is generic to both types of reforming. That work is still in progress, and shows substantial promise.

This report is organized as follows. The background section describes the industrial importance of hydrogen, the methods of producing it, and the shortcomings of current production methods. Section 3 describes the advantages of a promising embodiment of the molten carbonate approach to reforming. Section 4 describes use of an immobilized molten carbonate salt to

alleviate corrosion concerns, and compares it to the Regate process. Section 5 describes energy enhancements for both approaches.

2. BACKGROUND

Hydrogen is a major industrial commodity which plays an important role in many processes. It is almost always an intermediate, as opposed to an end product, and hence its central role is not well known to the public. The two major uses of hydrogen are in petroleum refining and fertilizer manufacture (NH_3). There are dozens of lesser uses, ranging from methanol and oxoalcohol manufacture to edible oil hydrogenation. Most of the hydrogen consumed in refineries is a byproduct from other refining operations, e.g., catalytic cracking. Thus the NH_3 industry is the leading consumer of manufactured hydrogen, as opposed to byproduct hydrogen.

Steam reforming is by far the dominant H_2 production technology, with partial oxidation (using pure O_2) a distant second. The feedstock for steam reforming can be natural gas, LPG, or naphtha.

The American Institute for Chemical Engineers (AIChE) sponsors a major symposium every year entitled, "Ammonia Plant and Related Facilities Safety." The proceedings of those symposia are the most comprehensive literature source for up-to-date information on steam reforming, and form the basis for much of the following information.

There are three characteristics of the steam reforming reaction of methane:

that result in processing difficulties. First, CH_4 is a relatively refractory gas; high temperatures are necessary to make the reform reaction proceed even in the presence of a catalyst. The reaction is endothermic; heat must be supplied at the required high temperature without adding undesirable components to the synthesis gas such as excess nitrogen. High concentration of CO can result in carbon deposition according to the reverse Boudouard reaction:

The current practice of reforming is to pass the reactants through catalyst-filled tubes that are radiantly heated from outside by combustion gases. The difficulties mentioned above lead to a number of trade-offs or problems. High reform temperatures are desirable from both equilibrium and kinetic considerations. High pressures, although adversely affecting equilibrium, are beneficial to kinetics. More important, high reform pressures are desired because it is more economical to pressurize the reform reactants than to compress the product hydrogen. However, the actual pressure and temperature must be traded off against metallurgical limitations. The current reformer tubes operate at the frontier of metallurgical capability -- 33 atmosphere and 870°C internal temperature. These tubes are made of a super-alloy such as HP 40: 25% Cr, 35% Ni, balance Fe. High temperature differences across the tube wall are used to minimize the required number of tubes for a given heat flux. Thus the combustion gas temperature is typically 980°C. These conditions yield a nominal tube life of 10 years.

Since the reform temperature is limited by tube metallurgy, it is necessary to add more than the stoichiometric amount of steam, both to ensure adequate conversion of methane and to guard against carbon deposition. The reform catalyst is deactivated by carbon deposition, which is promoted by lower temperatures. Current steam reformers use a steam-to-methane ratio of 3.2 to 3.6. The stoichiometric requirement is 1 for the reformer alone, or 2 for the combination of reformer plus shift converter:

The extra steam added in current reformers provides a margin against carbon deposition even under upset conditions. However, it represents an energy loss both in raising the steam and in providing the extra combustion necessary to heat it to 870°C. It also adds to the size and cost of downstream equipment.

Recently there has been a growing interest in lowering the steam/gas ratio to the reformer and thereby reducing the energy requirement of the process. Reductions from the normal range of 3.2 to 3.6 to as low as 2.5 have

been demonstrated. However, it is acknowledged that this causes operation nearer to carbon deposition conditions, higher tube temperatures and shortened tube life. The adverse consequences of a short excursion into the carbon deposition region, and the effect on the catalyst operation, have been described. This may only be minor carbon deposition. Minor carbon deposition on the catalyst can be removed by a regeneration technique requiring about 24 hours. However, if the buildup is severe enough to cause plugging, tube overheating will occur and the tube must be isolated or replaced.

3. MOLTEN CARBONATE REFORMER

This invention utilizes molten carbonate salt in lieu of conventional catalyst tubes as a reform reaction medium. Prior art patents which are relevant to the use of molten salt as a chemically reactive medium include the following: Bond et al., (US Patent 2,754,187) teach a process for converting normally gaseous hydrocarbons, optionally admixed with a minor portion of steam, to a mixture of H_2 and CO. The reactants are contacted with molten alkali carbonate in the temperature range of 760°C to 1095°C so as to produce alkali metal oxide, and the alkali metal oxide is separately contacted with submerged combustion gases to reconvert the oxide to carbonate.

Kepp et al., (US Patent 2,844,453) teach contacting normally gaseous hydrocarbons with alkali carbonate so as to form alkali metal oxide, and regenerating the oxide to carbonate by contact with hot flue gas.

McMahon et al., (US Patent 3,252,774) teach a salt reforming process wherein normally liquid hydrocarbon and steam are reformed by contact with alkali metal carbonate and hydroxide salt. The reaction heat is supplied indirectly to the salt by an external source. It is disclosed that methane reforming is at an infeasible level in 29 w/o Li_2CO_3 , 71 w/o Na_2CO_3 at a steam/carbon ratio below 2.2 and a temperature of 816°C.

Shalit et al., (US Patent 3,786,138) disclose producing pure hydrogen by reacting carbonaceous material and steam with alkali metal hydroxide which is

substantially free of alkali metal carbonate, and separately oxidizing part of the alkali metal hydroxide to alkali metal peroxide by contact with air.

Prior art patents which involve reacting solid carbonaceous materials with steam in the presence of molten alkali metal carbonate include US Patents 3,252,773, 3,708,270, and 3,740,103.

As detailed below, the molten carbonate reform invention provides a process and apparatus capable of reforming a mixture of steam and normally gaseous hydrocarbons (methane or natural gas) to synthesis gas at economically feasible yields (better than 65% methane conversion) and at economical steam/carbon ratios (1 to 3) using practical temperatures (below 930°C), and with economical salt regeneration.

3.1. Disclosure Of Molten Carbonate Reform Invention

The reform reactants, a mixture of gaseous hydrocarbon and steam having a steam/carbon ratio between 1 and 3, are reformed in a liquid medium consisting essentially of alkali metal carbonate and hydroxide salts. The melt is at least 30% each sodium and potassium cations, and between 5 and 30% hydroxide anions, balance carbonate (all percents are molar percents). Reform salt temperature is between 830 and 930°C. The salt is separately regenerated by heating to between 860 and 960°C by submerged combustion of fuel and oxidizer (e.g., air), for recycle to the reform reaction. The residence time of the reform reactants in contact with the salt, between about 1 and 20 seconds, is selected such that between 65 and 90% of the methane is reacted. Unreacted methane is separated from the synthesis gas after CO shift and CO₂ scrub, and then used as part of the fuel for the submerged combustion regeneration reactions, or is recycled to reactant CH₄. There is essentially no alkali metal oxide in the salt melt (less than 1 ppm) during reform or regeneration. The inclusion of cesium cations in the melt, up to about 25%, both improves the kinetics and lowers the melting point. Lithium cation lower the melting point but lengthen the residence time. Up to 5% barium cations is beneficial to kinetics.

The reform and regeneration reactions are conducted at approximately the same pressure in the range of 5 to 40 atmosphere. The hot combustion gas exiting the regeneration zone is preferably filtered and then work expanded.

When ammonia synthesis gas is the product, the air necessary for stoichiometric N_2 for the NH_3 is preferably introduced directly into the reform reaction zone with the reform reactants -- thus the salt reformer replaces both the primary and secondary conventional reformers, and the regeneration duty is lessened. The same compressor supplies both combustion air and reform air.

The compressed air for combustion including the N_2 for NH_3 stoichiometry is preferably heated above $600^\circ C$ by heat exchange with the hot synthesis gas. For safety reasons this is preferably done by a double indirect exchange. The double indirect exchange prevents a single leak from allowing mixing of hot syngas and hot compressed air.

When low steam/carbon ratios are used, e.g., 2 or less, there is greater potential for carbon deposition during cooldown of the synthesis gas. One means of avoiding this is to withdraw part of the reform salt, cool it to near the melting point by indirect heat exchange with compressed air and/or reform reactants, and then countercurrently contact it with the hot synthesis gas exiting the reformer. This both cools the synthesis gas and partially replaces the carbonaceous species (CO_2 and CO) with H_2O and H_2 , thus reducing the tendency to deposit carbon. This also reduces the downstream shift and scrub duties.

3.2. Brief Description of the Drawings

Figure 1 is a simplified schematic flowsheet of the molten carbonate reformer incorporating separate reform and regeneration zones, and the system for delivering hot pressurized reactants to each zone and recovering high temperature heat from the effluent from each zone. Figure 2 is a computer-generated heat and mass balance of the molten carbonate reformer.

3.3. Best Mode For Carrying Out The Invention

The molten carbonate reformer comprises an alkali carbonate salt melt contained in a pressure vessel lined with high-alumina refractory. The gas space above the melt is divided into separate reform and regeneration zones by a baffle; salt circulates freely under the baffle. Figure 1 illustrates the functioning of the reformer 1. A mixture of steam and methane is injected into the reform zone 2, and the synthesis gas is withdrawn at 3. Oxygen (air) plus any necessary fuel for heat addition is injected into the regeneration zone 4, and combustion exhaust is withdrawn at 5. The molten salt acts as a heat carrier, conveying reaction heat from the regeneration zone to the reforming zone, as a catalyst for the steam-methane reaction, and as a liquid seal to prevent the gases from mixing. There are effectively no metallurgical limits on temperature or pressure, as the pressure containment is cooled by refractory insulation. The operating temperature is substantially above the nominal 790°C of current reformers, thus improving equilibrium and reducing the steam requirement. Also, carbon deposition in the melt is not detrimental, and may even be turned to advantage.

Pressure is free to be optimized for the user process, because the vessel walls, cooled by refractory, can achieve great strength while retaining low cost carbon steel construction. Pressures between 5 and 40 atmospheres are contemplated, with 15 to 20 atmospheres preferred.

The remainder of Figure 1 illustrates one preferred method of delivering reactants and combustibles to the reform and regeneration zones respectively. The flowsheet depicts the ammonia synthesis gas case, i.e., sufficient air is introduced into the reform zone to yield a synthesis gas having approximate 3 to 1 ratio of H_2 to N_2 . Air is compressed in compressor 6, and then heated in exchange with hot synthesis gas in heat exchangers 7 and 8. Those exchangers are preferably of double wall type, with some intermediate fluid between the syngas pressure boundary and the air pressure boundary. The portion of compressed air to be used as combustion air is routed through switching filter

assembly 9, comprised of manifolds 10 and 11, plus filters 12 and 13. The two filters are alternately switched between upflow of combustion exhaust and downflow of compressed air. The upflow removes virtually all traces of salt from the exhaust, while cooling it to about 750°C for introduction to the expansion turbine 14. The downflow cleans accumulated salt from the filter and further preheats the combustion air. The two 4-valve manifolds accomplish the switching action. The filters may consist simply of random dumped ceramic packing, e.g., alumina Raschig rings.

Combustion air enters the regeneration zone through one or more lances 15. Fuel can share the same lance or preferably be introduced separately. The fuel should include some steam and be below 650°C to preclude carbon plugging of the lance. Similar considerations apply to reform reactants lance 16, receiving preheated steam and methane from heat exchanger 17.

At reaction pressures above about 10 atmosphere, the compressor would include at least one intercooler. The turbine preferably directly drives the compressor. The sensible heat remaining in the turbine exhaust is used to raise steam in waste heat boiler 18.

There are two distinct modes of operation of this reformer, which achieve different levels of energy savings. They are distinguished by the relative amounts of steam supplied to the reform zone and hydrocarbon supplied to the regeneration zone. At one extreme is the conventional combustion case. All heat added to the salt is derived from combustion of hydrocarbon supplied to the regeneration zone. The steam supplied to the reform zone is sufficient to keep the reform gas suitably outside carbon deposition conditions. Carbon formation will occur only during temporary upsets and there is no steady-state inventory of carbon in the melt.

At the other extreme, the hydrocarbon supply to the regeneration zone is completely eliminated, and the steam supply to the reform zone is substantially further reduced. Thus extensive carbon deposition into the melt occurs, and the carbon is transported by the melt to the regeneration zone, where it becomes the

fuel which is combusted by the air supply. At first this modification would not seem to save additional energy, since the hydrocarbon is merely being shifted from one salt zone to the other. The key beneficial result, however, is that now more of the total carbon inventory leaves as CO_2 in the exhaust gas, and hence there is less inventory of carbonaceous species (CO and CO_2) in the reformed gas. This means that less steam is required for downstream shift conversion and CO_2 removal.

In this latter mode, wherein there is continual generation of carbon internal to the melt, one concern is to prevent excessive accumulation of carbon in the reformer. Direct measurement of the carbon inventory would be very difficult. The planned solution is to monitor the regeneration exhaust for excess oxygen. Excess oxygen in the exhaust, e.g., 0.5 to 1%, signifies that all available carbon in the regenerator has been consumed and that no continuing buildup is in progress.

4. IMMOBILIZED MOLTEN CARBONATE REFORMER

The molten carbonate reform process as described in the preceding section has been shown to be technically valid and meritorious for energy conservation. However it entails high risk due to the corrosive character of the circulating molten salt. With current low natural gas prices, the economic benefits of the increased energy efficiency are not sufficient to induce the risk capital necessary to progress to prototype stage. Accordingly the technology sits on the shelf, ready to be resurrected in a higher energy cost era.

In order to salvage some practical energy conservation and economic benefit from the research investment, alternative approaches were sought which would yield the same kind of benefits as molten carbonate reforming, without the corrosive risk.

It was discovered that two generic approaches are possible for accomplishing steam reforming using molten carbonate salt. One is the "simultaneous" approach wherein reform and regeneration occur at the same time, but spatially separated, and the molten carbonate forms a liquid seal

separating the two compartments. The second approach is "sequential" wherein the separation between reform and regenerate is accomplished by the time difference rather than location difference. This approach has the disadvantage of intermittency, with the gas space alternately cycling between heavily reducing conditions and neutral conditions. However, since no liquid seal is required, nor is any circulation of the molten salt required, the sequential approach makes it possible to immobilize the molten carbonate on solid supports. This eliminates the biggest development risk in molten carbonate reforming - the corrosivity of the salt melt. The intermittency reduces the energy conservation potential, due to changeover losses. It also involves having the same vessel alternate between reducing conditions and neutral conditions with some danger that it could go to oxidizing during upsets. However that danger is in essence a control problem not unlike others routinely encountered in industry.

The primary conceptual effort in developing this cycle was working out the details of a two vessel version, wherein one vessel was in reform mode while the other regenerated, and then both reverse. That version was compared to a single vessel version, wherein traveling wave fronts were carefully controlled to allow both reactions to proceed in a single vessel. Additional effort was necessary on the gas supply and removal system, especially the work recovery expander (essentially a gas turbine).

As the conceptual work on the Immobilized Molten Carbonate Reformer process was completing, it was discovered that a competitor had already invented a similar process and was commencing development. A paper was published in the proceedings of the 1991 Ammonia Plant Safety Symposium on the Regate process. That paper is reproduced as Appendix 1.

The technical Paper, "Regate: a Process to Preheat Gases at High Temperature under High Pressures," was authored by the European company "Catalysts and Chemicals Europe SA." Although different from our process in several details, it nevertheless disclosed the basic concept of sequential reforming, with regeneration via combustion using pressurized air.

5. REFORMER HEAT AND WORK RECOVERY

There is a great deal of high temperature sensible heat available in the hot reformed gas plus hot combustion exhaust. Some (approximately 1/3) of that heat is used to preheat the reform reactants up to about 600°C, but the rest is used at low temperature (~ 320°C) to raise steam, plus a small fraction to superheat the steam.

Most processes requiring synthesis gas, and especially ammonia synthesis processes, require a great deal of shaft work to accomplish the various compression duties. Typically all of the steam generated from waste heat recovery is used, either for process reactant or for driving a steam turbine to produce the required shaft work. Thus although hypothetically it is possible to recover more high temperature heat by heat exchange between reform reactants and hot gases exiting the reformer, in practice there is no incentive to do so. The lesser amount of waste heat means less steam is generated, and the steam deficit would then have to be made up from some other source such as an auxiliary-fired boiler.

Using steam to generate the necessary shaft work requires almost 4 Joules of heat for every Joule of shaft work generated. Merely recovering more of the available high temperature waste heat at high temperatures provides no benefit such as increased steam generation or reduced fuel input requirement. What is needed is to recover more of the high temperature waste heat so as to more efficiently produce shaft work. That is one primary objective of the present invention.

It is known to provide fuel to a gas turbine to produce shaft work, and then to use the hot (~ 500°C) exhaust still containing about 14% O₂ as the combustion air for a reforming furnace. The three-quarters of the fuel energy that ends up as sensible heat of the turbine exhaust would otherwise have to be supplied at the reforming furnace. The one-quarter additional fuel energy ends up as shaft work (net gas turbine output). Although this is an efficient means of converting additional fuel to shaft work, it takes no added advantage of the existing high

temperature exit streams from the reformer, and hence tends to result in a steam excess. Also, the added gas turbine is a large capital expense, and it must compress about half again more air than the O_2 actually reaching the reforming furnace would indicate.

US Patent 4,337,170 discloses a steam reforming arrangement wherein two reformers in parallel are used -- one is heated conventionally by combustion gases, and the other, having a steam-carbon ratio between 3 and 6, is heated by the combined reformed gas discharged from both reformers. This provides a more effective recovery of high temperature waste heat, but does not either reduce the shaft work requirement or increase the efficiency of converting waste heat to shaft work.

In order to increase the recovery of high temperature reformer waste heat and more efficiently convert it to useful work the following procedure is proposed. Air is compressed, then indirectly heated by at least one of the hot reformed gas and the hot combustion exhaust, then work-expanded, and then supplied to the reformer furnace as combustion air.

The compressor is most conveniently driven directly by the turbine. For high compressor discharge pressures, e.g., above about 10 atmospheres, at least one stage of intercooling will normally be incorporated. When ammonia synthesis gas is being produced, the same compressor can supply part or all of that duty.

Heat exchange can economically heat the air to above $600^{\circ}C$, and in some cases to above $750^{\circ}C$. In some cases it will be desirable to add supplementary fuel to the heated compressed air to raise it to the allowable turbine inlet temperature, typically $900^{\circ}C$.

In general the turbine exhaust will be close to $500^{\circ}C$ and will contain close to 20% O_2 (usually 20.9%). Thus less air must be compressed to provide the furnace O_2 requirements, compared to prior art disclosures having about 15% O_2 . Also, the higher O_2 content provides hotter flames and better radiant heat transfer.

The heat exchange between compressed air and combustion exhaust may use any conventional means for heat exchange; brazed plate fin exchangers, shell and tube exchangers, fin tube thermosyphons, rotary wheels, and the like. One of the simplest and most economical designs consists of switching regenerator beds, such as are commonly found in cryogenic air separation plants and blast furnaces.

When heat is exchanged between compressed air and hot reformed gas, it is preferably a double indirect exchange for safety considerations, i.e., the compressed air and the reformed gas should not share a common pressure boundary. Double wall exchangers may be used, or other techniques meeting the double indirect criterion: fin tube thermosyphons (containing e.g., Na, K, or Cs); pumped liquid loops (molten carbonate salt or NaK), or even pumped molten salt loops in which one of the heat exchanges is via direct contact.

The greatest conversion of high temperature waste heat to useful shaft work will be obtained when turbine reheat is used: the compressed air is heated by one high temperature stream, partially expanded, then heated by the other stream, and then expansion is completed. To maximize work output, the pressure ratio across each turbine should be in the range of 3 to 8. Thus compressor discharge pressures of 10 to 60 atmospheres are in order. A discharge pressure of about 33 atmospheres to match the secondary air pressure requirement works particularly well.

When recovering high temperature heat from the hot reformed gas, it is desirable to maintain approximate water-gas-shift equilibrium. This preserves the greatest margin against carbon deposition, and has the added beneficial effect of releasing at least part of the water-gas-shift exothermic reaction heat at the useful high temperatures. Thus interspersing one or more small containers of appropriate HTS catalyst at appropriate high temperature locations in the heat exchange train is beneficial.

Further energy economy is obtainable by cooling the compressor inlet air below ambient using discharge waste heat as the mode of power. Work continues on this variation

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FIGURE 1

The diagram illustrates a fuel cell system. At the bottom, a large horizontal vessel contains two chambers: 'REGEN.' (left) and 'REFORM' (right). A central vertical tube separates them. Two electrodes, labeled 15 and 16, are submerged in the REGEN. chamber. A 'FUEL' inlet arrow points to electrode 15. A 'WATER' inlet arrow points to electrode 16. A line labeled 5 connects the REGEN. chamber to a diamond-shaped valve assembly 11. From valve 11, a line goes to a vertical cylinder 12. Another line from valve 11 goes to a second diamond-shaped valve assembly 10. From valve 10, a line goes to a vertical cylinder 13. A line labeled 14 connects cylinder 13 to a turbine 'T'. A line labeled 18 connects the turbine 'T' to an 'EXHAUST' outlet. A line labeled 6 connects the turbine 'T' to a compressor 'C'. An 'AIR' inlet arrow points to the compressor 'C'. From the compressor 'C', a line goes to a vertical cylinder 7. A line labeled 17 connects cylinder 7 to a vertical cylinder 8. A line labeled 3 connects cylinder 8 to the 'REFORM' chamber. A line labeled 16 connects the 'REFORM' chamber to a vertical cylinder 17. A line labeled 17 connects cylinder 17 to a vertical cylinder 7. A line labeled 7 connects cylinder 7 to a 'SYNGAS' outlet. A line labeled 17 connects cylinder 17 to a 'CH₄ + H₂O' outlet. A line labeled 17 connects cylinder 17 to a vertical cylinder 8. A line labeled 3 connects cylinder 8 to the 'REFORM' chamber.

EQUILIBRIUM HEAT AND MASS BALANCE

FIGURE 2

AIChE Meeting
Ammonia Plant Safety
Los Angeles Nov 17-22, 1991

Paper No. 281a.

THE REGATE : A PROCESS TO PREHEAT GASES AT HIGH TEMPERATURE UNDER HIGH PRESSURES

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abstract

- The REGATE is a cyclic thermal process which operates continuously and can preheat at high temperatures, up to 1600°C, and high pressures, up to 50 bars or more, many types of gases such as air, oxygen, nitrogen, carbon dioxide, steam or reducing gases (hydrogen, hydrogen rich gases, etc...).
- A schematic description of the system is given and the operation is explained.
- The process has been successfully experienced during several months in the fertilizer plant of MARLY (Brussels, Belgium) to preheat 1000 Nm³/h of air, steam and air-steam mixtures, up to 1300°C under 17 bars; during the last phase of experimentation, an autothermic reformer, connected to the REGATE, produced NH₃ synthesis gases from the air-steam mixtures preheated in the REGATE and from natural gas.
- A complete study of the REGATE has been made in conjunction with the use of turbines in order to optimize the thermal efficiency of the REGATE and the results of this study are given.
- The use of REGATE in ammonia plants has the following effects :
 - * reduction of energy consumption
 - * simplification, investment reductions
 - * increased capacities in existing plants
 - * possibility of high pressure operation
- Due to its flexibility, the process can be easily integrated in conventional existing plants and in new "low energy" plants (LCA, MERA, etc...); several examples of integration are given.

WHAT IS THE "REGATE" PROCESS ?

REGATE ^(R) is a cyclic and regenerative process to preheat process gases at high temperature (Fig. 1).

REGATE was originally developed by a group of Belgian companies and organizations (1).

The process was successfully demonstrated in 1986-87 during several months of continuous operation at the MARLY fertilizer plant (Brussels) by preheating 1000 Nm³/h air, steam and air-steam mixtures up to 1300 °C under 17 bar (Fig. 2).

During the last phase of the demonstration program, the REGATE unit was connected to a catalytic partial oxidation reactor and successfully produced ammonia synthesis gas from natural gas and air without any enrichment by oxygen.

- (1)
- CENTRE DE RECHERCHES METALLURGIQUES (Liège) : Joint research for iron and steel industry in the Benelux countries.
 - DISTRIGAZ (Brussels) : importation, storage and supply of all the natural gas used in Belgium.
 - S.B.A. CHIMIE/GECHM (Brussels) : ammonia, fertilizer and chemical products (until end 1987).
 - FABRICOM : technical venture and plants operations, active in many sectors including instrumentation, electricity, piping, heating, air conditioning.
 - CATALYSTS AND CHEMICALS EUROPE : catalyst production and development. Took over the rights of S.B.A. CHIMIE/GECHM in January 1990.

HOW DOES REGATE WORK ?

In principle REGATE works like the regenerators used in steel plants, but with two fundamental differences :

- the cycles are shorter (2-3 min. instead of 30);
- no valve is used on the hot gas exit line.

Essentially, REGATE ^(R) consists of two cylindrical reactors, A and B, both of which are refractory lined, filled with a suitable thermal mass and equipped with a heating burner (Fig. 3).

Each reactor is alternatively heated by the combustion of fuel gas, and then cooled by the process gas to be heated.

The operation is automatically controlled by the position of valves.

On Fig. 3, for instance, valves 1B, 2B and 3B are closed and valves 1A, 2A and 3A are open so that combustion occurs at the top of reactor A. The thermal mass A is heated and flue gas is extracted at the bottom of reactor A.

During the same period, valve 4A is closed and 4B is open so that process gas flows up through the bottom of reactor B and is heated by cooling the thermal mass B. Because the pressure in the system is carefully equalized there is no flow from reactor A to reactor B and vice-versa.

After a short cycle time (e.g. 3 min.), flue gas is blown out of reactor A with process gas, process gas flow is preheated in the thermal mass A and combustion is started to reheat reactor B.

Fig. 3

3. Because the high temperature reactors and connections are refractory lined, the pressure resistant points of the equipment are all at low or medium temperature. They can, therefore, be constructed with carbon steel with practically no pressure limitation.
4. When REGATE is used to heat process gases at medium or high pressure, the combustion air must be compressed to the same pressure as the process gas. A substantial amount of the conversion energy can, however, be recovered by expansion of the flue gas in gas turbines.
Fig. 5 shows the simplified arrangement of a combined REGATE/gas turbine system, and Fig. 6 shows the thermodynamic representation on the temperature-Entropy diagram.
This indicates that the thermodynamic cycle for combustion air/flue gas of REGATE corresponding to 1-2-3-5 can be broken down into two separate operations :
 - a classical gas turbine cycle corresponding to 1-2-2'-5;
 - a heating-cooling cycle according to 2'-3-4.

The first operation produces mechanical energy as is normal in a gas-turbine cycle.

The second supplies heat to the process at a high temperature level.

The use of turbines after a REGATE has been studied in cooperation with well known engineering specialized companies. For the purpose of the study only standard types of turbine have been considered. It was also concluded that small flow or temperature variations of the flue gases, or the presence of very small quantities of dust which might come from the thermal mass would cause no effect on the operation of the turbines.

Whereas energy problems are important in any modern chemical process, REGATE must be integrated with the process for an optimal thermodynamic result.

Among other things, the flue gas contains three potential energy sources :

- pressure,
- temperature,
- oxygen content.

This makes it possible - and highly profitable - to improve the performance of REGATE by the combination of high temperature expanders and gas turbines with one or more steps of post-combustion.

Fig. 7 shows one possible arrangement, and Fig. 8 translates this operation onto a temperature-Entropy diagram.

Table I illustrates the economics of such an arrangement and compares the energy costs of the process for different unit prices of electricity and natural gas.

Fig. 5

Fig. 6

Fig.7

Fig.8

**TABLE I. ENERGY BALANCE AND COST OF PRODUCTION
OF A REGATE UNIT**

1. Process conditions :			
Gas to be preheated :	air		
Flow (Nm ³ /h)	: 100,000		
Inlet T (°C)	: 250		
Exit T (°C)	: 1500		
Heat duty (GJ/h)	: 190		
2. Energy balance			
			<u>GJ/h</u>
- Fuel gas consumption (8250 Nm ³ /h)			295
(Nat.gas at 95% CH ₄ , 5 % N ₂ :			
(for REGATE heating and gas turbines)			
- Electric power :			
a) Combustion air			
compressor :	16200 kWh/h		
b) Energy recovery			
(turbines) :	<u>-27900</u> "		
balance	-11700 kWh/h		
or -	135 GJ/h (1)		<u>-135</u> (*)
- Net energy consumption			<u>160</u>
3. Costs (\$/h.)			
a. Unit costs			
- NG (\$/MMBTU, LHV)	2.75	2.75	1.75
- kWh (cents/kWh)	4	6	6
b. Total costs(\$/h)			
- NG consumption(fuel)	+ 770	+ 770	+ 490
- Electric power	<u>- 468</u>	<u>- 702</u>	<u>- 702</u>
TOTAL	+ 302	+ 68	- 212 (!)
c. Cost of heat			
supplied to the			
process (\$/MMBTU)	1.59	0.36	-1.12 (!)

(*) Base : 1 kWh produced with steam at 100 bars/510°C in condensation turbines needs 11.62 MJ

~~In other words,~~ Thanks to the mechanical energy produced by the gas turbine cycle, the net energy consumption (1) (160 GJ/h) is equal to 84 % of the heat supplied to the process at high temperature level (190 GJ/h). The economics are even more attractive when electricity is expensive and natural gas is cheap.

(1) Heating value of the natural gas to the REGATE and to the gas turbine less the steam value of the mechanical energy recovered.

REGATE ^(R) APPLICATIONS

Many industries consume thermal energy at high temperature and the higher the temperature, the better the performance of the installation.

This is true for the production of steel, glass, lime, cement and the operation of several chemical processes especially the production of ammonia synthesis gas.

To fully appreciate the potential of REGATE ^(R) in this field, it is useful to recall the recent evaluation of ammonia production techniques.

At the present time the most widely used process for producing ammonia synthesis gas consists in reacting hydrocarbons with steam at high temperature according to the reforming reaction :

This reaction is strongly endothermic so that not only should the reactants be preheated to the reaction temperature (800 °C), but it is also necessary to provide the heat absorbed during reaction. The simplest way to do this is to burn a part of the process gas with air in the reactor. The quantity of air should be sufficient to maintain the ratio of $\text{CO} + \text{H}_2/\text{N}_2$ at the outlet of the reactor close to the value required for ammonia synthesis. That is approximately 3.05.

Unfortunately the stoichiometric quantity of air is insufficient to give a high enough reactor outlet temperature to lower the residual methane level to the required value (950-1000 °C; 0.2 - 0.6 % CH_4).

For many years this difficulty was avoided by enriching air with oxygen, in autothermal catalytic reformers utilizing methane or heavier hydrocarbons low in sulphur, or by using pure oxygen, in non-catalytic autothermal cracking applied to heavy hydrocarbons with a high sulphur content (Fig. 9a).

AUTOTHERMAL CATALYTIC REFORMER

Fig. 9a

TUBULAR REFORMER

Fig. 9b

HEAT EXCHANGE REFORMER

These processes are relatively simple, reliable and easy to run, but are penalized by the cost of oxygen, and by the combustion in the reactor of an appreciable part of the process gas.

In the case of an autothermic reformer fed with enriched air about 20 % of the process gas is burnt to form CO_2 and H_2O .

To avoid these constraints, a part of the heat absorbed by the reforming reaction may be supplied by heat exchange tubular reforming furnaces where the combustion of a fuel, (normally natural gas) heats the outside of vertical tubes through which the hydrocarbon-steam mixture flows. The tubes are filled with a nickel catalyst.

Reformed gas leaves the tubes at about 800°C with a residual methane content of about 10 %. The gas then passes through an adiabatic secondary reformer, in which the additional heat of reaction is supplied by partial oxidation with added air (fig 9b).

Under primary and secondary reforming conditions the stoichiometric quantity of air is sufficient and extra oxygen is not required.

At the present time this type of process is universally applied in the form of large size units (1000-1500 MT NH_3 /day).

However, such units present a certain number of well-known disadvantages :

- performance is limited by the strength of the reforming tubes which are, simultaneously, submitted to high temperatures and pressures;
- working close to the admissible limits, the reforming furnace represents a vulnerable piece of equipment, with high investment and maintenance cost; because of the thermal limitations, start-ups are long and costly;
- only half of the heat produced in the primary reformer furnace transfers to the process gas, the rest leaving in the flue gas at 1000°C ; the economics of the process require the recovery of this energy in a complex and expensive system of exchangers and heaters;
- a large part of the heat in flue gas must be recovered as steam which must be reused in complex systems which are integrated in the unit.

Since the first single stream units of 1000 ST/D capacity were constructed in the 1960's, many process improvements have been introduced to lower the role of the tubular primary reformer.

Amongst others :

- higher secondary air temperatures (from 450°C up to 800°C).
- secondary air flows greater than the stoichiometric requirement combined with less severe operation of the primary reformer (for instance operation at a primary outlet temperature of 700°C with a methane leakage of up to 25%). Excess N_2 and CH_4 are then removed by a cryogenic system or molecular sieves.

It appears that the latest "low-energy" units have almost reached the thermodynamic limits of the existing process.

The gains which can still be achieved in the performance of these units will remain marginal and limited, for instance, by the behaviour of special steels under pressure and at very high temperature.

Older process routes, which have been abandoned for several decades, should now be re-examined to design units which :

- . are simple;
- . have lower investment and maintenance costs;
- . have equal or lower energy consumption than the latest "low-energy" units;
- . are economic with small design capacity.

Recent developments and studies have introduced processes in which the hot gas leaving the secondary reformer heats the reforming tubes of a high pressure reformer (heat exchange reformer) (fig 9c).

As a result, the reforming furnace can be eliminated together with all the problems associated with it.

However, the amount of heat which can normally be recovered from the secondary reformer outlet gas can only supply about 60% of the heat required by the primary reforming reactor with the other 40% being supplied in one of the following ways :

- . by a conventional primary reformer;
- . by enriching the secondary reformer air with oxygen;
- . by using an excess of air in the secondary reformer followed by a downstream cryogenic unit or molecular sieves to remove excess nitrogen.

The use of the REGATE^(R) preheater represents a new and better solution of this problem.

In the case of a catalytic autothermal reformer (Fig. 9a) by increasing the temperature of the steam/air/oxygen mixture, and maintaining the temperature at the autothermal reactor exit constant (eg 950°C) the oxygen enrichment of the air can be progressively reduced.

Fig. 10

Fig. 10

With an overall S/C ratio of 3 the process can operate with air alone when the preheat temperature reaches 1600°C. At a S/C ratio of 4.0 the same result will be achieved with a preheat temperature of 1400°C.

In other words, the introduction of the REGATE^(R) preheater permits the production of an ammonia synthesis gas (fig 11a)

- IN A CATALYTIC AUTOTHERMAL REFORMER
- WITHOUT OXYGEN ENRICHMENT OF THE AIR
- WITHOUT A TUBULAR REFORMER
- WITHOUT THE ADDITION OF A CRYOGENIC OR MOLECULAR SIEVE SEPARATION SYSTEM.

When combined with an efficient thermodynamic cycle, as shown in Fig 7, and when this cycle is properly integrated into the chemical process, the combination REGATE-CATALYTIC AUTOTHERMAL REFORMER, operating with air, leads to the development of units which are more economical than the best existing ones.

APPLICATIONS

In the present state of ammonia plants and for their development the REGATE preheater can be used for the following applications:

I. REVAMPING OF EXISTING UNITS

Catalytic autothermic reformer

The addition of a REGATE would allow (fig 11a):

- . reduction or even elimination of oxygen enrichment;
- . increase in capacity, possibly combined with the preceding advantage.

Tubular reforming

The replacement of an existing primary reformer by a REGATE is theoretically possible but might be considered too adventurous due to the risk and the complexity of the integration. Such possibilities should be studied case by case.

Interesting results can however, be obtained by installing a REGATE to preheat process air (fig 11b). This does not require any major change in the unit but merely the insertion of a REGATE between the outlet of the existing process air preheater and the secondary reformer.

The top of the secondary reformer needs also to be adapted.

The Process air temperature can then be raised from the normal temperature of 450-600°C up to 1200 - 1500°C. This extra heat to the secondary reformer can be used profitably in various ways to :

- reduce the severity of the primary reformer operating conditions and increase tube-life;
- reduce the methane concentration in reformed gas if there is a benefit in reducing purge from the synthesis loop;
- reduce the S/C ratio;
- above all increase reformed gas production by 20-30%. This can be achieved by injecting supplementary natural gas into the secondary reformer, with the correspondingly increased quantities of air and steam duly heated to the high temperature in the REGATE with the main air stream.

In fact, simulations carried out on a 1200 t/D flow sheet show that an optimum condition can be achieved by combining these various advantages in a balanced way.

The REGATE allows debottlenecking in the reforming section without changing the load of the primary reforming-furnace. Combined with new or existing techniques for improving operation of the CO conversion section, of the CO₂ removal system and of the ammonia synthesis loop, the complete revamping of existing units can be made with a maximum of safety.

REGATE + AUTOTHERMAL CATALYTIC REFORMER

Fig. 11a

REGATE + TUBULAR REFORMER

Fig. 11b

REGATE + HEAT EXCHANGE REFORMER

Examples of revamping of existing reforming units

Table II compares an existing plant (Reference) with various cases of revamping with REGATE.

Reference : Typical ammonia plant with :

- primary reformer (800°C; S/C = 3.5; P = 33 bars a; NG = 95% CH₄, 1% C₂H₆, 4% N₂)
- H.T. and L.T. conversion (0,2% CO), CO₂ removal (0,1% CO₂) methanation
- no molecular sieves or cryogenic treatment of syngas
- no separation unit on purge gas (20% CH₄ + A)
- classical HP steam recovery (100 bar a) and power production by HP steam turbine (100 to 35 bar a) and MP steam condensation turbines.

Case A1 : same as reference case, except :

- heating process air to 1500°C by REGATE;
- S/C down to 2,7.

Results :

- a) primary reformer heat duty down to 84% of reference case;
- b) slight increase of ammonia production;
- c) 8% reduction of energy costs; reduction of direct and indirects maintenance costs (tube life).

Case A2 : same as case A1 except :

- increasing heat duty to the value of reference case;
- additional process NG and steam to the primary reformer to balance the new heat duty (+ 19% of the value of reference case).

Results :

- a) general heat duty of the primary reformer (radiant section and conversion section) almost the same as reference case;
- b) 8% reduction of energy costs;
- c) increase of the ammonia production to 120% of the reference case.

Case B1 : same situation for primary reformer as for case A1 but :

- additional process NG directly to the secondary reformer (+ 30%)
- total process air plus corresponding additional process steam (for S/C = 2,7) to the REGATE

Results :

- a) primary reformer heat duty down to 84% of Reference case;
- b) increase of ammonia production (130% of reference case);
- c) 11% reduction of energy costs; reduction of direct and indirect maintenance costs (tube life).

Case B2 : same as B1 except :

- increasing heat duty close to the value of reference case with additional process NG and steam to the primary reformer to balance the new heat duty (+ 15% of the value of the reference case);
- proportional increase of the additional process NG to the secondary reformer and of the additional process steam to the REGATE.

Results :

- a) general heat duty of the primary reformer (radiant section and convection section) almost the same as reference case;
- b) 11% reduction of energy costs;
- c) increase of the ammonia production to 150% of reference case.

PROFITS : the results on table II are calculated for two situations :

- a) selling price of ammonia equals the actual cost of production;
- b) selling price of ammonia equals 110% of the actual cost of production.

They do not include the charges (depreciation and financial costs) of the new investments (REGATE and debottlenecking).

A complete calculation can only be done case by case for existing situation with additional optimization of the results.

Table II gives only a first idea of the possibilities of the new process.

**TABLE II. REVAMPING OF THE REFORMING SECTION OF AN
EXISTING AMMONIA PLANT WITH REGATE**

	REFERENCE	A1	A2	B1	B2
PROCESS CONDITIONS					
S/C	3.5	2.7	2.7	2.7	2.7
Process NG					
- to prim.reform.(kmol/s)	0.4449	0.4449	0.5278	0.4449	0.5116
- to sec.reform. "	-	-	-	0.1335	0.1535
Process Steam					
- to prim.reform.(kmol/s)	1.5106	1.1653	1.3823	1.1653	1.3401
- to REGATE "	-	-	-	0.3497	0.4021
Process air					
- to sec.reform. (kmol/s)	0.5719	-	-	-	-
- to REGATE "	-	0.5752	0.6824	0.7433	0.8818
Primary Reformer					
- outlet temp. (°C)	800	800	800	800	800
CH ₄ (mol %)	11.25	15.50	15.50	15.50	15.50
- heat to the tubes (KJ/s)	84840	72715	84840	73211	84200
Regate					
- inlet temp. (°C)	(534)	498	498	363	363
- outlet temp. (°C)	(534)	1500	1500	1500	1500
- heat exchanged (KJ/s)	0	19610	23260	45931	52820
Secondary Reformer					
- outlet temp. (°C)	968	1076	1076	1023	1023
CH ₄ (mol %)	0.30	0.11	0.11	0.23	0.23
NH ₃ product (kmol/s)	0.9401	0.9135	1.0837	1.1747	1.3509
(Mt/d)	<u>1330</u>	<u>1344</u>	<u>1594</u>	<u>1729</u>	<u>1988</u>
ENERGY BALANCE (1)					
NG process (GJ/t NH ₃)	22.42	22.19	22.19	22.44	22.44
fuel prim. ref.	8.86	7.40	7.40	5.24	5.24
REGATE + gas turb.	0	2.24	2.24	4.07	4.07
	31.28	31.83	31.83	31.75	31.75
Electricity (Kwh/t NH ₃)	36	-98	-98	-132	-132
equiv. (GJ/t NH ₃)(2)	0.42	-1.14	-1.14	-1.54	-1.54
Total Energy (GJ/t NH ₃)	31.70	30.69	30.69	30.20	30.20
COSTS					
Cost of production					
N.G. (3) (\$/t NH ₃)	81.01	82.44	82.44	82.23	82.23
Electricity (3) "	2.16	-5.88	-5.88	-7.92	-7.92
Miscellaneous	2.00	2.00	2.00	2.00	2.00
	85.17	78.56	78.56	76.31	76.31
Fixed costs (4) (\$/t NH ₃)	50.00	49.48	41.72	38.46	33.45
	135.17	128.04	120.28	114.77	109.76
Annual profit (5) (MM\$)					
a) if S.P. = 135,17 \$/t	0	3.1	7.8	11.6	16.7
b) if S.P. = 135,17 + 10%	5.9	9.2	14.9	19.3	25.5

(1) GJ LHV / Mt ammonia.

(2) 11620 KJ/kwh

(3) Unit cost : 2.75 \$/MMBTu, LHV or 2.59 \$/GJ LHV; 6 cents/kwh

(4) Included catalyst, manpower, administration, maintenance, insurance, financial cost, residual depreciation.

BUT not included : depreciation and financial costs related to the REGATE and revamping investment.

(5) a) Selling price = actual cost of production; production 330 d/y;

II. NEW PLANTS

REGATE opens the way for AMMONIA PLANTS WITHOUT TUBULAR REFORMING AND WITHOUT A CRYOGENIC OXYGEN-PRODUCTION UNIT (fig 11a) OR ANY KIND OF NITROGEN SEPARATION UNITS.

With the benefits of the thermodynamic cycle on the flue gas expansion, and with a rigorous energy integration, it is possible to design ammonia lines which are competitive with current "low-energy" plants both in terms of investment and energy consumption.

A recent study on a low energy ammonia process (Ref 1) showed that :

- (a) the primary reformer waste-heat section only preheats natural gas, reformer feed, process air and combustion air. No heat is supplied to the steam system;
- (b) all economic heat available downstream the secondary reformer, from the shift converters and from the synthesis loop, is recovered for high-pressure superheated steam production (about 3t/t NH_3);
- (c) this steam is sufficient to drive the syngas compressor, the process air compressor and the boiler feed-water pump.

If the primary reformer is replaced by a REGATE, with the associated compressor, turbines and heat exchangers (fig. 12); the REGATE could feed the existing secondary reformer with air, steam and gas in such conditions that the exit gas from this "autothermic reformer" has the same temperature and composition as the low energy process.

The results are given in table III.

CONVENTIONAL "LOW ENERGY" 1000 MT NH₃/d

LOW ENERGY" WITH REGATE 1000 MT NH₃/d

(x) 1 kWh = 2750 kcal ; 1 kg STEAM (40 kg/cm g ; 380°C) = 757 kcal

Fig. 12

TABLE III. ENERGY BALANCE (GJ LHV/1 Mt NH ₃ - 33°C) Capac. 1000 Mt NH ₃ /d						
	PRESENT "LOW ENERGY"			"LOW ENERGY" + REGATE		
1. <u>Energy balance</u>						
NG Process	+ 21.98	GJ/Mt NH ₃		+ 21.98	GJ/Mt NH ₃	
NG Fuel(Regate + turbines)	+ 5.86	" "		+ 10.34	" "	
Steam export (1)	- 0.42	" "		- 0.42	" "	
Power import (1)	+ 0.50	" "		+ 0.50	" "	
Power export (Regate) (1)	-			- 4.73	" "	
	<hr/>			<hr/>		
	27.92	" "		27.67	" "	
2. <u>Economics</u>						
a) <u>Unit costs :</u>						
- NG (\$/MMBTU, LHV)	2.75	2.75	1.75	2.75	2.75	1.75
- kWh(cents/kWh)	4	6	6	4	6	6
b) <u>Energy cost (\$/Mt NH₃)</u>						
- NG process	57.3	57.3	36.5	57.3	57.3	36.5
- NG fuel	15.3	15.3	9.7	27.0	27.0	17.2
- Steam export	-1.1	-1.1	-0.7	-1.1	-1.1	-0.7
- Electric power import/export	1.7	2.6	2.6	-14.6	-21.8	-21.8
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
Total energy cost (US\$/Mt NH ₃)	73.2	74.1	48.1	68.6	61.4	31.2

(1) 1 kWh = 3.6 MJ; 1 kg steam (40 bar : 380°C) = 3.17 MJ.

Table III shows that with the REGATE it is possible to produce NH₃ with a total energy consumption of 27.67 GJ (LHV)/Mt NH₃ and that, by comparison with the present "low energy" technology the advantage of the REGATE is particularly interesting when electricity is expensive and the natural gas is at low cost.

MISCELLANEOUS REMARKS :

The REGATE process presents other advantages which cannot be developed extensively in this paper

1. A REGATE cycle may be combined with a prereformer with improved results.
2. To improve the operation of systems using the HEAT EXCHANGE REFORMER concept, it is possible to eliminate the thermal deficiency of this type of process by preheating process air to the secondary reformer to an appropriate temperature in a REGATE (Fig 11c).
3. It should be emphasized that the high temperature sections of the REGATE are refractory lined, and that the high pressure resistance of the equipment can be ensured by carbon steel working at moderate temperatures. There is, therefore, nothing to prevent synthesis gas generation at pressures of 80-100 bar. This would be impossible for tubular reforming.
In view of recent technical innovations in the fields of CO conversion, CO₂ removal, and ammonia synthesis, there is no obstacle to the design of a MONO-PRESSURE AMMONIA PLANT, WITH COMPLETE ELIMINATION OF SYNTHESIS GAS COMPRESSION.
4. With a REGATE and in absence of a primary tubular reformer, heavier hydrocarbons and sulfur containing feeds can be much more easily reformed.
5. When all the ammonia production is to be converted into urea, carbon dioxide from the CO₂ removal section may be insufficient to balance the ammonia production. With REGATE, it is possible to recover carbon dioxide under pressure from the flue gas of the REGATE with practically no additional energy consumption.
6. With some minor modifications to meet safety requirements, REGATE can also be used to preheat at high temperatures gases containing H₂ and CO. It can also be used as a cyclic catalytic reactor working at high pressure.
7. The investment cost of REGATE and associated turbines and heat exchangers is roughly 60 % of the investment of a primary reformer with waste heat recovery.

All these possibilities and many other arrangements of REGATE combined with various processes have been studied to demonstrate the economic validity of the system. Detailed calculations have yet to be done case by case on specific problems.

Ref 1. "Advances in Ammonia Production Technology" by
Dr.Ib. BYBKJAER / H. Topsoe AS
Presented at 1990 FAI Seminar
New Dehli, India