

Steam Naphtha Reforming By The Imperial Chemical Industries Process

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In 1803 Thomas Robert Malthus published his "Essay on Population" which culminated a five year study of population growth in all the countries of the world. Malthus concluded that population tends to grow at a rate faster than the rate of growth of food producing resources and that therefore famines, wars and pestilence were an unavoidable means of checking this growth. Malthus' pessimistic view of the future was borne out in the 1800's by the Napoleonic wars followed by food shortages in Europe and the Irish famine of the 1840's.

Some 70 to 80 years later Sir William Crooks, the eminent English chemist who discovered the element thallium, predicted that the entire world faced a wheat famine in 25 years because existing supplies of nitrogenous fertilizers (Chilean saltpeter) would be exhausted by that time. Sir Crooks stated: "The fixation of atmospheric nitrogen is one of the greatest discoveries awaiting the ingenuity of chemists". (1)

Now, after another period of some 70 to 80 years, attention is again being directed to the age old problem of producing enough food to support the world's growing population. The emphasis has passed, however, from the prevention of starvation to maintaining and, hopefully, to improving the diet of undernourished millions, and as well as to planning the use of raw material resources to feed the burgeoning population of the world. (2)

That the emphasis has shifted reflects with credit upon advances in science. The use of manures and composts for improving the yield of farm products dates from the earliest days of civilization. In the second century before Christ, Cato, in his book De re Rustica, detailed the benefits to be derived from organic fertilizers. Arab scholars in the 10th Century noted the value of blood as manure - suggesting that human blood was the best kind. American Indians placed fish in their corn hills.

Lacking, however, was the scientific approach that would lead to recognition of the value of inorganic sources of soil nutrients. Obviously, organic material was limited in availability. The first scientific efforts were undertaken by John Bennett Lawes at his estate, Rothamsted.

Lawes studied chemistry at Oxford and was well versed in the theoretical discussions of contemporary chemists on the subject of soil management. He determined to perform practical application work on his estate, tackling as his first problem the making of water soluble soil nutrients.

By extensive experimentation in pots and then in the open soil of the fields, Lawes found that bones needed a preliminary treatment with acid to consistently achieve

their maximum effectiveness. In 1842 he patented a process for treating bones and rock phosphate with sulfuric acid to make soluble phosphates.

By about 1880, application of Chilean nitrates to the soil was accepted, and shipment of nitrates expanded 10 fold in the subsequent 30 years. (3) With this as the background, the stage was set for some scientist to synthesize ammonia.

One likes to think that the ability to synthesize ammonia opened a new era of well being for mankind. Unfortunately, nitrogenous compounds were as vitally important to the waging of war, at least before the atom bomb, as they were to the growing of food. Within 4 years after successful laboratory synthesis of ammonia by Fritz Haber, World War I was declared.

The production of nitrogen from various sources before and after World War I is shown in Table I.

In 1913, production of nitrogen totalled 851 thousand tons. In 1918, production had increased 38% to 1160 thousand tons. In the same 5 year interval of time, production of synthetic nitrogen increased 700% from 3% to 16% of the total production.

Germany was the only nation to achieve self-sufficiency in nitrogen required for both explosives and fertilizers. The United States did not have an ammonia synthesis plant in production until 1921.

With the importance of fertilizers now scientifically demonstrated, and with techniques available to synthesize ammonia from the plentiful supplies of nitrogen in the atmosphere, attention was directed to alternate sources of, and economic means for recovering, hydrogen.

In these early years, the various sources of hydrogen were limited to byproduct gas from the electrolysis of brine, byproduct gas from the conversion of coal to coke and "producer gas" from the reaction of incandescent coke with steam.

Considerable work was being done on the reforming of gaseous hydrocarbons by the I. G. Farben interests. (4) Basic patents were issued in 1913 and 1927. Following an exchange of information with Standard Oil Development Company (now Esso Research & Engineering Co.), Standard Oil brought the process to commercial realization in 1930 with an installation of three reformers at their Bayway, New Jersey Refinery. Three more installations were made soon thereafter at their Baton Rouge, Louisiana Refinery. Standard Oil's installations were for the purpose of producing hydrogen to hydrogenate low quality gasolines, kerosenes and diesel fuels. It appeared that hydrogenation of distillate oil stocks would be a major process for all refiners because of the relatively poor quality crude oils available at the time.

Concurrent with Standard's interest, Imperial Chemical Industries in 1928 undertook pilot plant studies of steam reforming of gaseous hydrocarbons. These studies led to a commercial installation in 1936.

In the latter part of the Thirties, Standard Oil's interest in the process waned as the need for oil hydrogenation processes failed to materialize. However, ICI continued their intensive pilot plant work, as their prime interest was ammonia production and they recognized the importance of steam reforming in the preparation of ammonia synthesis gas.

The United States chemical companies were not unaware of the potential for steam reforming. Both Hercules Powder Company and Atlas Powder Company approached I. G.

Farben in the latter part of the 1930's for knowhow and rights to build reforming furnaces. Both companies were rejected (3). Hercules proceeded to develop its own reforming catalyst and furnace, starting up a small plant in 1940.

At the outbreak of World War II, the United States ammonia industry was ill-equipped to handle the quantity of nitrogen required to support the war effort, since the major producers of ammonia, DuPont at Belle, West Virginia and Allied Chemical at Hopewell, Virginia were still dependent upon coke for hydrogen. There were seven other plants--all quite small. Five used electrolytic hydrogen, one cracked refinery gases and one reformed natural gas. Consequently, the U. S. government had constructed ten new ammonia plants with an estimated annual productive capacity of 800,000 to 900,000 tons per year of nitrogen--more than twice the productive capacity of the plants then in operation (3).

Of the ten new plants built by the Government, six were based on steam methane reforming. ICI loaned a team of engineers to cooperate in the construction of three of the reforming plants, and undoubtedly the ICI knowhow was of influence on the design of the other three reforming plants.

ICI's interest in reforming of hydrocarbons was not limited to gaseous hydrocarbons. As early as 1938, ICI had demonstrated the ability to reform sulfur-free distillate hydrocarbons. This technique was not commercially applied until 1954 when a plant at Heysham, England was adapted to reform a sulfur-free synthetic hydrogenated gasoline with a 192°C end point. After development of a sulfur removal process, this plant was converted to reform straight run distillate fractions with the same end point.

The early naphtha reforming plants operated at low pressure, but further development work led to a pressure process which permitted reforming up to 400 pounds pressure at steam to carbon (mol) ratios comparable to those used in steam methane reforming.

The success of the ICI Steam Naphtha Reforming Process is being demonstrated today by ICI's own construction program. Practically all ICI's capacity to produce ammonia and methanol synthesis gas is already converted from coke to naphtha reforming. Additional ammonia plants based on naphtha reforming are planned or under construction.

Furthermore 13 towns gas plants producing a 400-500 Btu per cubic foot gas from naphtha are operating or under construction in Great Britain.

Reforming Reactions

The reactions occurring in steam naphtha reforming are basically the same as those in steam methane reforming, with the addition of a series of reactions, extremely complex due to the length and configuration of the carbon chain of the heavy hydrocarbons making up the naphtha fraction.

The pertinent reactions are shown in Table II. In reaction 1, substitution of methane (CH_4) for C_nH_m yields a statement of the overall reaction for steam methane reforming. In all probability the actual reaction mechanism consists of a cracking-dehydrogenation reaction, which produces carbon, and a concurrent and competing reaction of carbon with steam to yield hydrogen and the carbon oxides.

In the case of a naphtha containing various paraffinic, aromatic and naphthenic compounds having a boiling range encompassing C_4 to C_{10} fractions, the complexity of the reaction mechanism increases greatly.

The ability of the reforming process to operate successfully depends upon the avoidance of carbon laydown. Two mechanisms for carbon laydown can be identified: one based on the equilibrium relations expressed by equations (2.), (3.) and (4.) in Table II, and the other based on the cracking-hydrogenation-polymerization reactions of the hydrocarbon.

In the case of the first mechanism, based on the reaction of an average light distillate hydrocarbon with steam, ICI has computed a tendency to form carbon in the range of 1000 to 1200°F. This carbon forming reaction takes place very rapidly in the presence of nickel catalyst. In this temperature range, should the steam rate be reduced below a certain minimum, carbon forms instantaneously throughout each catalyst pellet causing the pellet to disintegrate.

The second carbon forming mechanism is believed to occur as a result of a cracking-dehydrogenation reaction, followed by polymerization to tarry substances which, in turn, carbonize to a soft sooty carbon. This carbon forms on the exterior of the catalyst not within the interstices. No damage to the catalyst results from this carbon deposition. The active surface of the catalyst is blanketed, thereby reducing its activity and also building up pressure drop through the catalyst bed. This type of carbon can be removed by oxidation (i.e. regeneration with steam and air) without impairment of catalyst activity or physical strength. Prevention of carbon is a matter of maintaining suitable steam ratios and keeping the reactants in contact with the catalyst. Care must be exercised in loading the catalyst so that bridging is avoided.

Reaction 1, in Table II is a highly endothermic reaction. Reaction 3, which is the well known water-gas shift reaction, is exothermic. This, coupled with the complexity of the feed analysis and the potential for carbon deposition, makes necessary the selective use of a catalyst which promotes the desired reactions while also inhibiting the reactions leading to carbon deposition. It also necessitates precise control of the heat input profile to the tubes of the reformer.

Reformed gas from the naphtha reformer consists of hydrogen, carbon dioxide, carbon monoxide, methane and traces of heavier gaseous hydrocarbons. Feed naphtha is completely converted. The presence of methane in the gas results from either, or both, the initial cracking reaction of the naphtha or reaction 2 (shown in Table II) which is the reverse of the steam methane reforming reaction.

The ICI Process

The ICI process consists of sulfur removal and steam reforming over a special ICI catalyst, followed by conventional processing techniques to make hydrogen synthesis gas for ammonia or methanol and towns gas.

Sulfur removal is fundamental to the successful performance of the ICI reforming catalyst, as the catalyst is sulfur sensitive. A three-bed desulfurization process is usually required. The first bed is a bed of zinc oxide; the second bed a cobalt molybdate catalyst; the third bed another bed of zinc oxide.

Elemental sulfur and hydrogen sulfide are absorbed by the zinc oxide. Mercaptan and disulfide sulfur, in the presence of hydrocarbons and zinc oxide, are converted to hydrogen sulfide, which is then absorbed by the zinc oxide. Thioethers are also hydrogenated to hydrogen sulfide and similarly removed. Other sulfur compounds are non-reactive in the presence of zinc oxide and are hydrogenated over cobalt molybdate catalyst to hydrogen sulfide, which is removed in the final zinc oxide bed. The sulfur concentration in the feed to the reformer is reduced to between 3 and 5 parts per million.

The zinc sulfide formed in the above process must be periodically replaced. In the case of naphthas with high sulfur content, it may be economic to use preliminary electrostatic acid treatment to remove most of the sulfur before the three-bed treatment.

After desulfurization, the vaporized naphtha passes to the steam reformer where it is admixed with steam and converted to a hydrogen-rich gas. The steam reformer is the heart of the process. Suspended in the center of its firebox are vertical tubes packed with catalyst. These suspended tubes are heated externally by a large number of burners. Advancement in furnace design and tube metallurgy have gone hand in hand with advancements in catalyst technology. Reformers today not only can reform liquid fractions but also produce at higher space velocities, with higher flux densities and higher tube wall temperatures than have been considered for methane reforming.

A simple outline drawing of a typical steam reformer is shown in Figure I. Desulfurized, vaporized naphtha flows down through a bed of catalyst contained in a multitude of tubes. Because the reactions occurring at the top of the tube are highly endothermic, a large quantity of heat must be contributed to the reaction to prevent carbon laydown. Various furnace designs accomplish this in different ways. (4) In the furnace design shown (Selas Corporation of America), the variable heat input down the length of the tube is accomplished through the use of a multiple number of radiant cup burners arranged in horizontal rows which can be independently fired to give the optimum heat profile.

The tube wall temperatures of a naphtha reformer will operate in the range of 1700 to 1750°F. The generally accepted technique for manufacture of the catalyst tubes is permanent-mold centrifugal casting of a Type 310 stainless steel (ASTM 297-55 HK). The grain formation is such that the tubes have higher stress values than the extruded tubes.

Despite the greater carbon laydown potential of naphthas relative to gaseous hydrocarbons, the ICI catalyst is able to operate continuously without carbon laydown or loss of activity, even at operating conditions more severe than those of conventional steam methane reforming. Current designs are based on a 3 to 1 steam to carbon mol ratio and 400 pounds pressure. Outlet temperatures, determined by the desired effluent gas composition, range from 1200 to 1500°F. Straight-run naphthas with end points as high as 400°F can be reformed. There is no restriction on the degree of aromaticity.

Application Of The ICI Process

The applications of the ICI Steam Naphtha Reforming Process are the same as those of the conventional steam methane reforming process. The process produces a hydrogen-rich stream containing, as impurities, carbon dioxide, carbon monoxide, methane and traces of heavier gaseous hydrocarbons. This stream is subsequently processed by conventional techniques to give either a relatively pure hydrogen, a hydrogen-nitrogen mixture for ammonia synthesis, hydrogen-methane mixture for town gas, or a hydrogen-carbon oxide mixture for methanol or oxo chemicals manufacture.

Block-flow diagrams are shown in Figure II to delineate the fundamental differences of processing schemes for hydrogen, ammonia synthesis gas and town gas manufacture.

The scheme for hydrogen generation includes sulfur removal, the primary reforming reaction, shift conversion (where the carbon monoxide is reacted with steam to produce more hydrogen and carbon dioxide), and purification to remove carbon dioxide and to methanate the residual quantities of the carbon oxides back to methane by

reaction with hydrogen (a reversal of the reforming reaction). The resultant final product has only parts per million of the carbon oxides which are catalyst poisons in most processes that require hydrogen. The reforming operation will be at temperatures sufficiently severe to minimize the methane in the outlet of the reforming process. The concentration of methane will usually be of the order of 1 to 4% depending upon the ultimate use of the hydrogen.

The scheme for ammonia synthesis differs from the hydrogen generating scheme by the addition of a secondary reformer which combusts part of the product stream with air. The secondary reformer introduces the nitrogen required to yield a 3 to 1 hydrogen-nitrogen mixture which, after purification, goes to an ammonia synthesis converter.

It is obviously not necessary to reform the naphtha as severely in this scheme, since a certain amount of residual hydrocarbon can be used to combust with air. Under the less severe operating conditions, the methane content in the product from the reformer will be in the range of 7 to 10%. It is interesting to note that, even in cases where the reforming is not done under severe conditions, naphtha does not show up in the product from the reforming step.

In the secondary reformer, after combustion, the gases pass through a catalyst bed that further reduces the methane content. The secondary reformer is a refractory-lined vessel which operates at a temperature higher than the outlet temperature of the primary reformer, thereby making it possible to achieve concentrations of methane in the product as low as one-quarter of one percent.

The balance of the processing steps are similar to hydrogen manufacture, i.e. shift conversion and purification.

In the production of towns gas, the process scheme varies greatly with the final specifications of the towns gas. In principle however, as shown in Figure II, a low-severity reforming and shift conversion step is required. Addition of an enrichment gas is also required, and some balance must be struck between carbon dioxide removal and inert gas makeup.

Naphtha Reforming Vs. Steam Reforming

At the present time, the determinant for using Naphtha Reforming instead of Steam Reforming is more one of raw material availability than one of economics. In major market areas of the world, natural gas either does not occur or has not been discovered and developed. In these areas natural gas can only be made available by liquification and tanker shipment. The economies of these areas are therefore oriented around oils for heating and, to an ever decreasing extent, around coal. Naphthas are usually in long supply, as the gasoline consumption is not great enough to absorb them. Here the ICI Steam Naphtha Reforming process has its broadest application.

On the other hand in an economy built around natural gas as a fuel, and with a large automobile population as is the case in the United States, naphthas as a raw material for reforming are too expensive relative to natural gas.

To demonstrate the relative values of naphtha and natural gas as raw materials for reforming data have been developed from a recently published paper on the economics of reforming (5). By comparing the relative requirement of feed and fuel for naphtha reforming and methane reforming a breakeven curve has been plotted as shown in Figure III.

In Great Britain, which conforms to the condition of an oil-based or coal-based economy, lacking natural gas resources, naphthas in large quantities can be contracted for at a price of about 0.8 cents per pound. The breakeven value of natural gas is 47-48 cents per million Btu--not an unusually high price in terms of the U. S. economy, but without significance in Great Britain where the gas is not naturally available.

However, in the case of the United States which is the largest natural-gas-fuel-based economy having a large automobile population, naphthas on the East Coast sell in the range 1.5 cents per pound. The natural gas breakeven is about 90 cents per million Btu, or just about double the going market price for natural gas.

The United States economy, with respect to sources and uses of natural gas, automobile population, and refining capacity is a mature enough economy that no unusual dislocation of this price structure is anticipated. Such is not the case in many of the major market areas such as Great Britain. Extensive discoveries of natural gas in Holland and the North Sea could have a significant bearing on the future economics of the entire European area.

To the extent that natural gas replaced fuel oil for heating purposes, crude oil runs would be reduced, thus reducing the surplus of naphtha. The expanding automobile population of Europe would absorb more of the naphthas. The net result would be firming of the price for naphtha.

In view of the potentially unstable fuel economy in Europe, many naphtha reforming projects under bid require rating of the naphtha reforming equipment on natural gas. The ICI process is readily converted to methane reforming.

Basic to naphtha reforming are the following processing steps not required by methane reforming:

1. Desulfurization. Either a fixed bed or combination of electrostatic acid treating and a fixed bed.
2. Vaporization facilities for naphtha.
3. Imperial Chemical Industries naphtha reforming catalyst.
4. Larger capacity facilities for carbon dioxide removal.

Were a naphtha reforming plant to be converted to methane reforming, the acid-treating sulfur removal step and the naphtha vaporizer could be dispensed with. The fixed-bed desulfurizer could be used for removal of sulfur from the natural gas, although the desulfurizer would be grossly oversized. The ICI catalyst will reform methane equally well as naphtha. Carbon Dioxide removal facilities would be oversized, since the less favorable carbon-to-hydrogen ratio of naphtha, relative to methane, result in the production of more carbon dioxide per unit of product. (See Table III)

In the case of capital investment, it has been shown (5) that the battery limits cost for an ammonia plant based on naphtha reforming is about 18% greater than for one based on methane reforming. For a plant to produce 97% purity hydrogen, the naphtha reforming plant investment is about 30% greater than that of one based on methane reforming. It should be noted that although the two percentage figures are different by a large degree, nevertheless the order-of-magnitude differences of the absolute values are roughly comparable, since the ammonia plant cost includes the cost of the

ammonia synthesis loop. Technological advances in the ICI process during the past year have resulted in pressing the technological frontier back faster than methane reforming, and the spread between the costs for naphtha reforming and methane reforming are probably somewhat diminished today.

Conclusion

Science has demonstrated over the years the ability to develop new technologies to meet the ever increasing demands of population for food.

What once was a problem of elimination of starvation has now become a problem of maintenance, and improvement, of a minimum diet.

Technologies have been developed which free the world from the uneconomic restrictions on the use of raw materials to manufacture fertilizers. Development of oil resources, shipping facilities and technologies, such as the Imperial Chemical Industries Steam Naphtha Reforming Process, permit the construction of economic facilities for ammonia manufacture anywhere in the world.

The problem of carbon deposition when reforming liquid fractions has been solved by the development of the ICI catalyst. Continued development work on naphtha reforming has pushed naphtha reforming technology beyond methane reforming technology, and furnaces are now being designed at higher space velocities, higher pressures, high tube wall temperatures and high heat flux densities.

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TABLE IProduction of Nitrogen From Various Sources Before And After World War I

	<u>Thousands of tons of nitrogen</u>	
	<u>1913</u>	<u>1919</u>
Chilean Nitrate	473	487
By Product Nitrogen	313	402
Cyanamide Nitrogen	42	98
Synthetic Nitrogen	<u>24</u>	<u>172</u>
	852	1159

TABLE IIReactions

- $C_nH_m + nH_2O = n CO + \frac{2n + m}{2} H_2$
- $CO + 3H_2 = CH_4 + H_2O$
- $CO + H_2O = CO_2 + H_2$
- $2CO = CO_2 + C$

TABLE IIICarbon Dioxide Produced By Reforming Reactions

Hydrogen Production - 97%	tons CO ₂ / M SCF H ₂
Steam Methane Reforming	14.51
Steam Naphtha Reforming	17.90
Ammonia Synthesis Gas Production	tons CO ₂ /ton ammonia
Steam Methane Reforming	1.22
Steam Naphtha Reforming	1.58

Figure I

Design of Selsas Corporation of America Steam Reformer

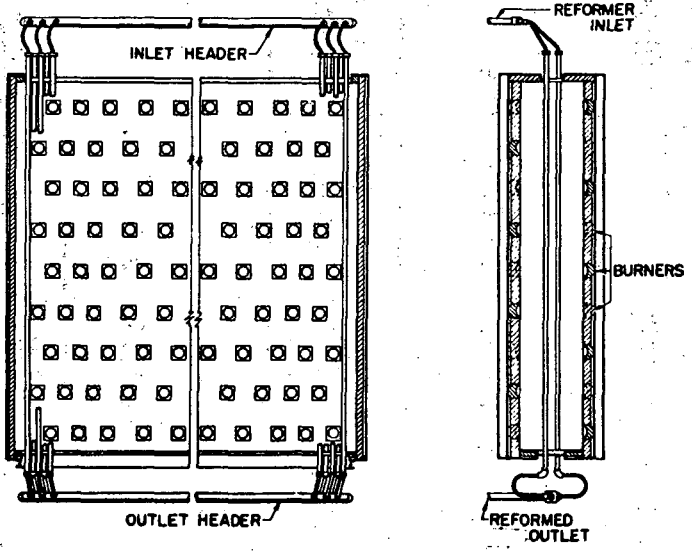
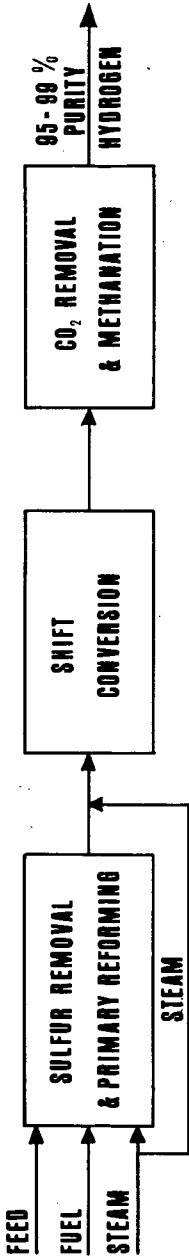
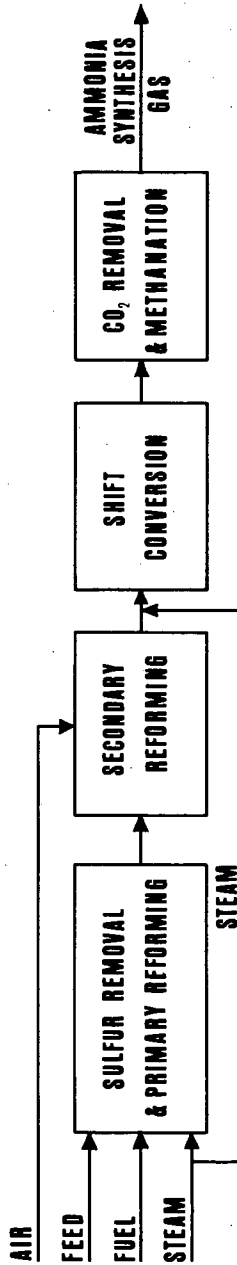


FIGURE 2

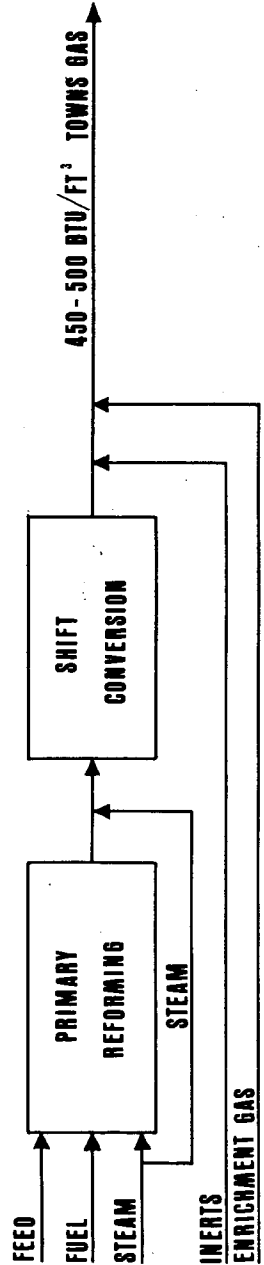
HYDROGEN PRODUCTION



AMMONIA SYNTHESIS GAS GENERATION



TOWNS GAS GENERATION



**Breakeven costs of feed & fuel: naphtha
reforming vs. methane reforming**

