

Recent Trends in Hydrogen Plant Technology¹

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Abstract

The catalytic reforming process for producing hydrogen for the vegetable oil and other industries is reviewed. The chemistry of the steam-hydrocarbon process and the present status as practiced in the U.S. are outlined. Results of research and development work are presented and a new process utilizing the Girdler "modular" reformer is compared to standard designs. The advantages of "low-temp" carbon monoxide conversion are also discussed. The importance of considering the safety and reliability of new designs is stressed.

Introduction

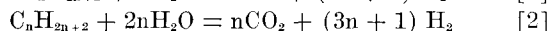
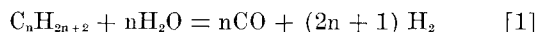
AFTER MANY YEARS of relative stability in the design of hydrogen plants, the industry is now undergoing revisions leading to a new era of cheaper hydrogen produced in more compact plants with greater ease and safety of operation. The new designs are the result of intensive research and development and engineering efforts directed toward utilization of new raw materials and more economical processes.

The impetus behind these developments is the spectacular upswing in hydrogen consumption demonstrated in this country and throughout the world. Hydrogen consumption in this country in 1961 was estimated at nearly 610 billion ft³ (1). Further estimates place consumption at nearly a trillion ft³ by 1970 (2). By far the major portion of this production goes into ammonia, methanol and petroleum refining operations. These uses are chiefly responsible for the continued rise in hydrogen consumption. Hydrogenation of oils is another substantial hydrogen customer. Although not currently undergoing a rapid expansion, this industry will remain a large user of hydrogen and therefore has an abiding interest in the development of cheaper hydrogen production.

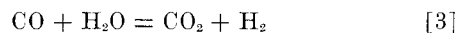
This paper discusses the new developments in the catalytic process for the manufacture of hydrogen from hydrocarbons and steam. The overall process is presented with a flow sheet and discussions of the chemical reactions and the process variables. Emphasis is placed on a new reforming process with modular design reformer and the new low-temp shift converter. Safety aspects of hydrogen plant design conclude the paper.

Chemistry of Hydrogen Manufacture

The steam-hydrocarbon process, commonly referred to as steam reforming of hydrocarbons, is based on the following reactions:



These reactions are endothermic, and are carried out at elevated temp in the presence of nickel catalysts. Reaction [2] may be considered Reaction [1] followed by the exothermic shift reaction:



The equilibrium constants for methane reacting according to Reactions [1] and [2] and for Reaction [3] have been reported for temp up to 2200F (3,4). The equilibrium constants for Reactions [1] and [2] increase with increasing temp and for Reaction [3] decreases with increasing temp.

Reactions [1] and [2] both result in volume increases and, therefore, proceed more completely at low pressures. For example, in Reaction [1] using methane, the amt of unreacted methane remaining is proportional to the square of the pressure at any given temp. Since hydrogen is

frequently used at elevated pressure, production at as high a pressure as possible is advantageous. The adverse effects of pressure on the reforming reaction are overcome by increasing the operating temp, or by increasing the ratio of steam to hydrocarbon, both of which will increase the extent of the reaction.

The conversion of hydrocarbons to hydrogen and carbon dioxide is ordinarily carried out in two steps. In the first step, in which the reforming Reactions [1] and [2] are carried out, the reactants flow through catalyst-filled tubes suspended in a furnace chamber. The operating temp is usually 1250-1700F and is maintained as high as possible with the available alloy steels from which the catalyst tubes are made. In the second step, in which the shift Reaction [3] takes place, the reactants flow through an adiabatic catalyst bed. The temp is usually between 350 and 800F since the equilibrium in this reaction is more favorable at lower temp. The catalyst used for this reaction is an iron oxide-chromium oxide mixture and the reaction rate attainable with these catalysts sets the lower temp limit of the process.

The carbon dioxide present in the product hydrogen stream may be removed by any suitable process, such as absorption by scrubbing with monoethanolamine, water or potassium carbonate. If it is desired to reduce the level of carbon oxides to parts per million, the hydrogen may be passed over a nickel catalyst at temperatures of 500-700F. At these conditions the equilibrium of Reactions [1] and [2] is reversed and the carbon oxides are hydrogenated to methane.

Process Description

A typical flow diagram for a hydrogen plant to produce hydrogen with as little as 0.5% methane shows in Figure 1. This plant uses steam-hydrocarbon reforming, a single stage of carbon monoxide shift conversion, amine scrubbing for bulk carbon dioxide removal and methanation for residual carbon oxides reduction to less than 10 ppm. The methane content of the hydrogen from the plant, as illustrated, may be varied according to operating conditions from a min of 0.5% up to 10 or 15%. This is in contrast with a min of ca. 2.0% methane in the product from existing single stage hydrogen plants. The higher purity product is made possible by a new process using the modular reformer which produces lower methane in the raw hydrogen and the new low-temp shift conversion which results in lower carbon monoxide.

To take full advantage of the new design concepts, the hydrocarbon feed gas should be compressed to 175-300 psig. Generation of hydrogen at elevated pressures has a number of advantages including a) lower plant pressure drop, b) smaller equipment, c) lower power when high pressure hydrogen is needed, and d) more available heat recovery. The compressed hydrocarbon feed gas is then passed over activated carbon for removal of organic sulfur compounds as these materials tend to reduce the activity of the nickel reforming catalyst. The desulfurization drums are operated at ambient temp and are periodically removed from service for regeneration by high-temp steaming. The desulfurized hydrocarbon and the steam required for reforming are then heat exchanged with the hot reformed process gas.

The superheated steam-hydrocarbon mixture then flows through the reformer tubes where the degree of removal of methane by reforming to hydrogen and carbon oxides sets a limit on the purity of the final hydrogen product. The reformer may be adjusted for lower residual methane by using a higher temp, a greater steam-hydrocarbon ratio or lower space velocity.

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The reformer effluent will contain much of the potential hydrogen product in the form of carbon monoxide which is next reacted with steam in the shift converter to complete the generation of hydrogen. Prior to entering the shift converter the hot reformer effluent must be cooled to the shift temp. This may be accomplished advantageously by quenching with condensate and heat exchange to the reformer feed and/or the methanator feed. The additional steam generated in the process gas favors the carbon monoxide shift reaction by a) increasing the activity of the reactants and b) limiting the temp rise and thus improving the equilibrium constant. For high purity hydrogen it is important that the residual carbon monoxide be low since in the final methanation clean up each volume of carbon monoxide reacts with three volumes of hydrogen.

The process gas from the shift converter contains mainly hydrogen, carbon dioxide and steam. In plants utilizing elevated pressure operation, the partial pressure of steam may be 50-100 psi and therefore is an excellent source of heat for stripping the carbon dioxide from the amine solution. Frequently, the operating conditions of the plant can be adjusted so that sufficient heat is available in the process gas for the amine regeneration.

In order to prevent excessive temp in the reboiler, the incoming process gas is usually quenched to nearly saturation by the addition of condensate. The steam condensed in the reboiler is collected and provides the condensate for quenching.

The carbon dioxide is removed by absorption in 15-20% ethanolamine solution in a packed tower. Other aqueous absorbents may be used, but if high purity hydrogen is required, ethanolamine is preferred due to its low equilibrium carbon dioxide vapor pressure and its relatively high mass transfer coefficient. It is important to remove the carbon dioxide to as low a value as possible since upon methanation, each volume reacts with four volumes of hydrogen.

The scrubbed hydrogen, now containing as low as 0.05% methane, 0.3% carbon monoxide and 0.1% carbon dioxide, is heated and passed through the methanation catalyst to yield approx 99.5% hydrogen containing less than 10 ppm carbon oxides.

New Girdler Reforming Process

A plant designed according to the flow diagram in Figure 1 would incorporate many design improvements representing the summation of engineering efforts over a period of years (5). The most significant improvements, however, are the newly developed Girdler reforming process with modular reformer and the low-temp conversion.

During the past 25 years reformers of conventional design incorporated catalyst filled tubes 25-30 ft in length hanging vertically in a large furnace chamber. Worthwhile improvements have been made to the original designs such as better alloys for the tubes, higher reforming pressures and more efficient heat utilization, but the size and shape have remained substantially unchanged.

Since the reformer is a major part of the capital cost of a hydrogen plant, we have undertaken an extensive program aimed at improving the efficiency and consequently lowering the cost of the reforming furnace. To this end the program has included investigations of such factors as size and placement of the reformer tubes, refractory and furnace wall construction, burner location and characteristics, and choice of catalyst and operating conditions. As a result, a new reforming process has been developed. This includes new process know-how as well as a new concept in reforming furnace design.

This advanced design is referred to as the Girdler modular reformer. This term is derived from the fact that the furnace is assembled from standard sections or modules. Incorporated in the design of such a unit are such features as the use of precast refractory panels in lieu of masonry construction, simplification of the inlet and outlet manifolding system, use of shorter reformer tubes, and employment of more active and more selective reforming catalyst.

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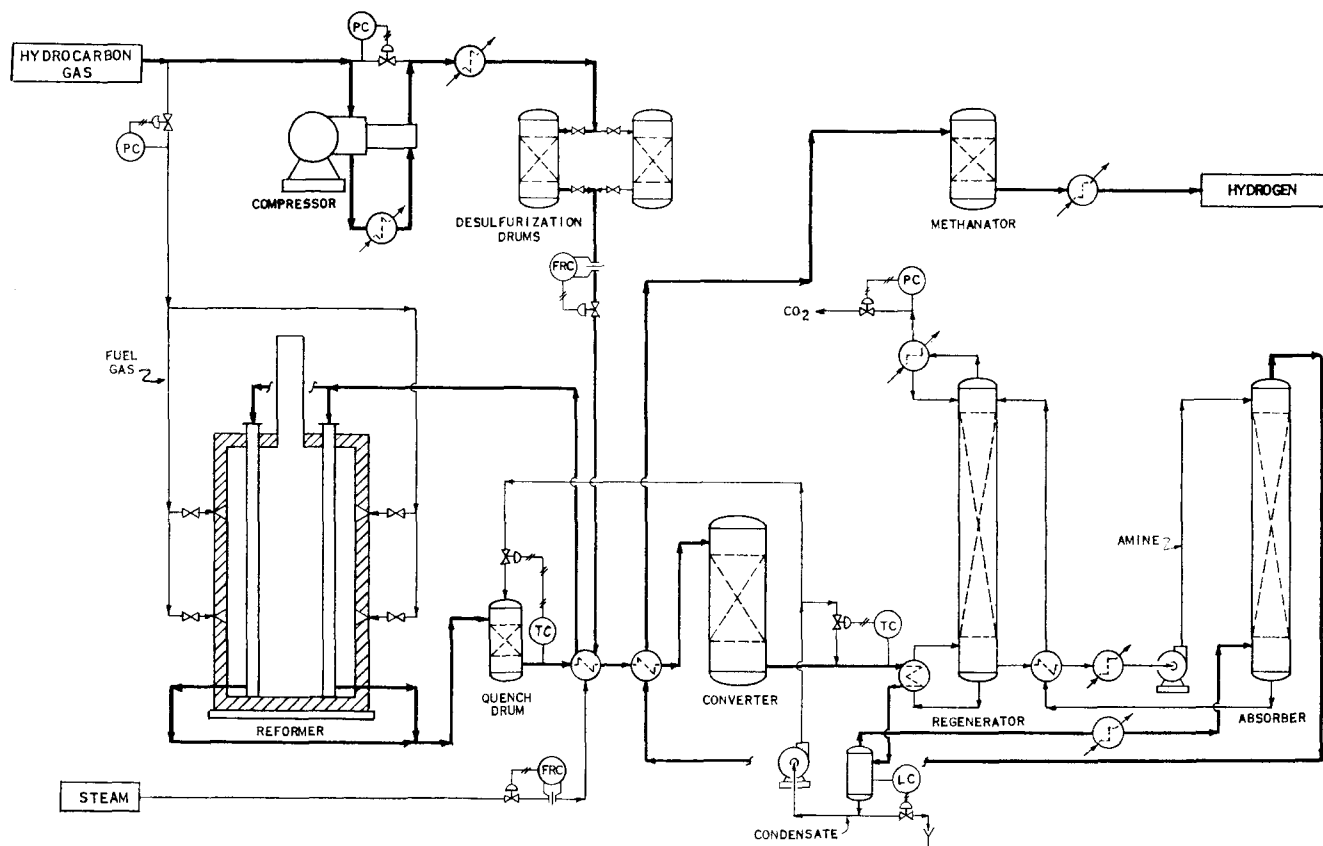


Fig. 1. Hydrogen plant process flow diagram.

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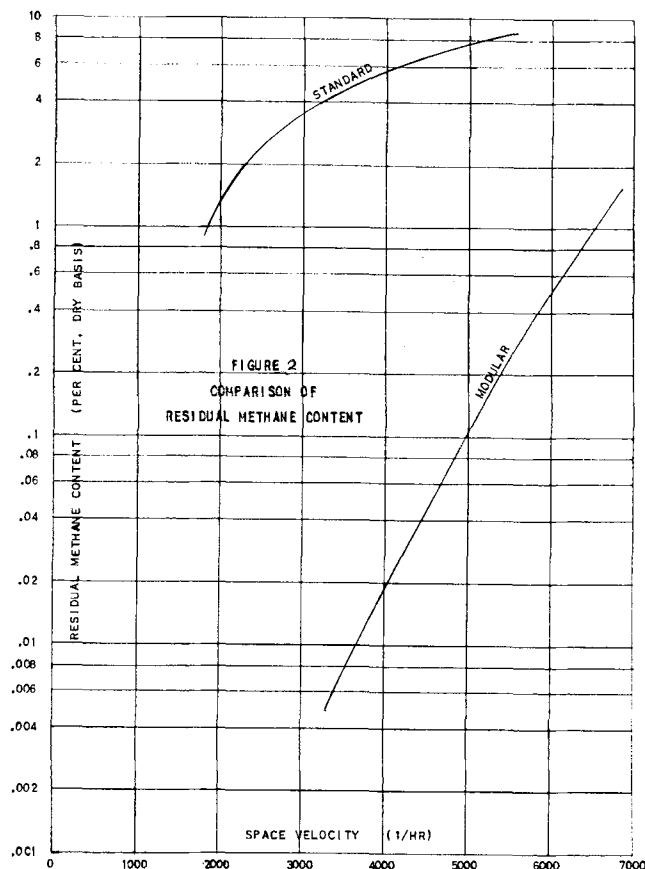


FIG. 2.

A prototype of the new reformer was constructed and the new process was operated over a period of 18 months in a pilot plant. Results have been most gratifying. Referring to Figure 2 which shows the relationship between the percentage of methane in the outlet gas and the space velocity, it is readily apparent that the new process and reformer are decidedly superior to the standard design. For any desired space velocity, a considerably smaller residual methane content is obtained or, conversely, for any given methane content, a greater allowable space velocity may be used.

Figure 3, which shows the relationship between the internal heat flux and the space velocity, depicts the greater heat flux obtained by the new process as compared with the standard process. Of particular note is the close approach to 100% of theoretical conversion. From this it may be seen that the new design permits the flow of sufficient heat into the catalyst tubes to bring about almost complete conversion of the feed material over a much broader range.

Another very important advantage of the new reforming process is its ability to handle a wide variety of hydrocarbon feed materials, ranging from methane to naphtha. In all instances, the performance of the new reformer was found to be considerably better than the standard designs now widely used in the industry.

There are considerable dimensional differences between the Girdler modular reformer and a standard unit of the same capacity. Thus, the standard reformer required to produce 25,000 SCFH hydrogen would have a base of 8 x 13.5 ft and an overall height of 48 ft, while the modular reformer requires a base of 8 x 12.5 ft and an overall height of only 12 ft. The compact size and inherent ruggedness of the new reformer make it an ideal unit for skid mounting in capacities up to 150,000 SCFH. Figure 4 is a photograph of a 25,000 SCFH modular reformer on skids and ready for loading on a truck or railroad flat car.

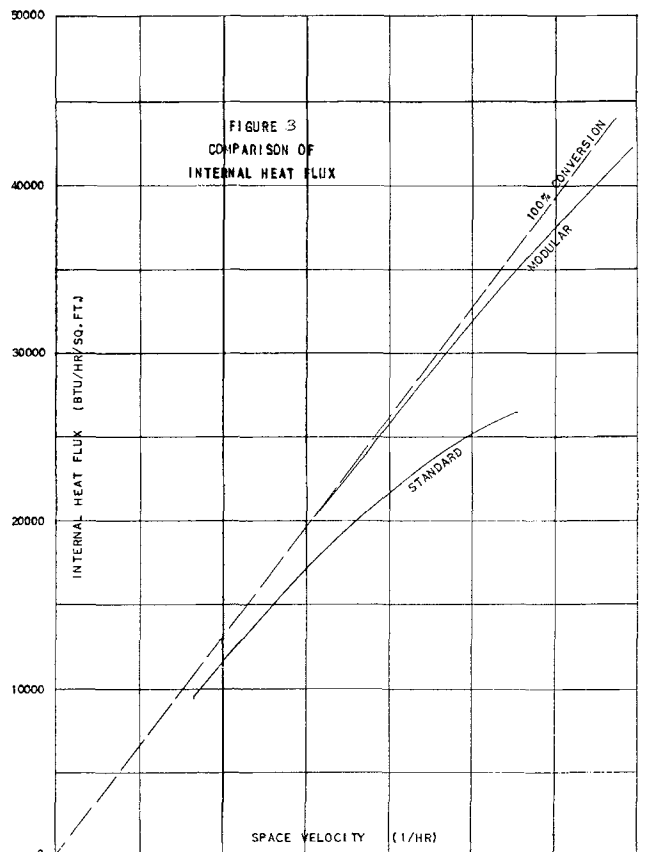


FIG. 3.

Low Temperature Conversion

The preceding discussion has pointed out that equilibrium of the catalytic shift reaction is favored by low temp and that the reaction rate attainable sets the lower temp limit. Heretofore most carbon monoxide shift reactors have been designed for operation at 650-850F. A single stage of shift could reduce the carbon monoxide to 1.6-2.5%. For further reduction a second stage could be used to reduce the carbon monoxide to 0.2-0.4%. However, before going to the second stage the gas must be cooled, the carbon dioxide removed and the gas then reheated to the shift reaction temp.

More active carbon monoxide shift catalysts are now available allowing operation at 350-400F with single stage carbon monoxide content at 0.2-0.4% (6). The recommended space velocity for a single stage low-temp plant is such that approx the same volume of catalyst is used as in a two-stage higher temp plant. However, the one stage plant allows a reduction in the number of towers, vessels, heat exchangers and pumps. In addition there can be a considerable saving in steam consumption.

Safety and Reliability

The basic selection of equipment for the production of hydrogen is governed to a great extent by degree of reliability. While technological advances in recent years have permitted commercial plant operations formerly considered impractical, each new advance must be considered in relation to the overall system. A rigorous set of engineering standards prepared by experienced engineers is essential as criteria for assuring reliability and safety in new designs.

The reformer tubes are subjected to the most extreme conditions in a hydrogen plant. Tube wall temp of 1600-1750F are quite common, while pressures range from near atmospheric to 450 psig. High quality chrome nickel steels such as 25-20 are essential due to their superior strength and creep characteristics at high temp and their corrosion resistance. Welding procedures are critical and detailed inspection and analyses are performed to maintain the highest degree of reliability. The tube assembly must be properly supported to allow for thermal expansion without caus-

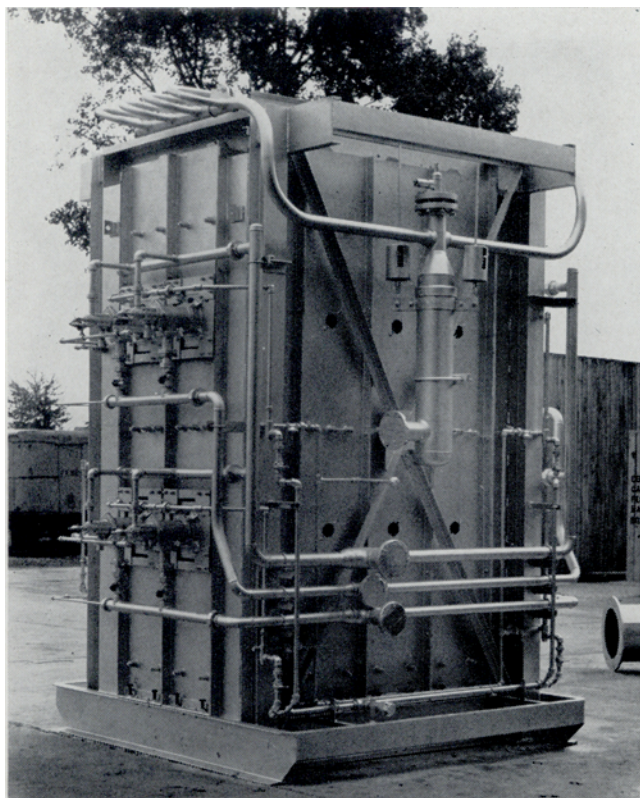


FIG. 4. Girdler Corp. modular reformer.

ing warpage of the tubes. Furnace firing methods must eliminate flame impingement and localized hot spots to prevent premature tube failure. With proper design and operation the tube life can be extended over a number of years. Actual operating plant data indicate that 10-20 years service is possible.

In recent years considerably more emphasis has been placed on operator and maintenance training as a means toward greater reliability and safety. In such programs, emergency procedures are stressed particularly on shutdown, purging and general safety practices, as well as routine operations.

A well-designed safety shutdown system can be a great value in preventing dangerous situations in the event of equipment failure or operating errors. Frequently, flame-sensing devices are installed in the reforming furnace which will alarm or shut down the firing system in the event of flame failure. Automatic purging cycles prevent the possibility of forming explosive mixtures in the fuel lines or firing chamber during startup and shutdown. Temp scanning devices can be provided to prevent localized overheating within the fired zone of the furnace.

Ratio flow controllers are used to control the proportion of reactants entering the reforming system. In the event of failure of the natural gas or steam supply an automatic shutdown system will prevent potential damage to the equipment. Strategically placed monitors can detect leakage of combustibles in critical areas.

It should be emphasized that no safety system can eliminate every conceivable hazard. Safety systems can also be over designed to the extent that stable operation is impossible due to premature shutdowns. The ultimate reliance must be on the well trained operator.

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