New Developments in Hydrogen Gas Generation Molecular Sieves[1]

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Abstract

The use of molecular sieves as a means of purifying steam-reformed hydrocarbon fuel in the production of low cost hydrogen has been developed into a practical gas generator design. Conventional processes for producing hydrogen are reviewed, with a history of molecular sieves and how this dry desiccant material was applied to commercial equipment as an adsorbent for removal of CO_2 and water vapor. The molecular sieve type hydrogen gas generator is discussed with an outline of typical operating cost and gas purity capabilities.

Introduction

In past years there have been several methods of producing hydrogen gas from gaseous hydrocarbon fuels, each developed to achieve optimim operating economics consistent with equipment cost, production dependability and maintenance.

The art of steam reformer and shift converter design for reaction efficiency has been substantially improved over the years, so that today a single stage train of equipment can be designed to yield a final hydrogen product well in excess of 99% purity. These accomplishments are due in large part to improved catalyst materials and present knowledge of their most effective use.

Fuels, such as natural gas or propane, are thermally treated in the presence of steam to reform the gas into two major constituents, hydrogen and carbon dioxide. By subsequent removal of the carbon dioxide, a final product of hydrogen gas is recovered for process use.

Conventional Purifiers

A number of systems for continuous removal of carbon dioxide have been developed in the past, including water absorption, caustic absorption and ethanolamine chemical absorption. These are generally classified as wet absorption systems. Due to factors of efficiency, equipment complexity and problems of corrosion and maintenance, ethanolamine systems have generally proven to be the most popular compromise. The majority of CO_2 scrubbing systems in recent years have used an aqueous solution of monoethanolamine (MEA).

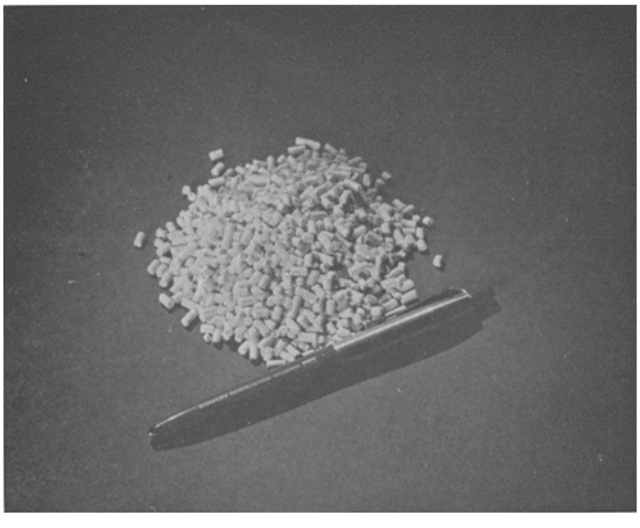

FIG. 1. Synthetic zeolite material.

The search for better carbon dioxide removal equipment has continued despite the fact that MEA systems have been improved to a point where residual CO_2 can be reduced to levels of less than 0.1%, and that effective corrosion inhibitors have become available to improve operating reliability.

One such new system is palladium diffusion purification. In this process a hydrogen-bearing gas is impressed under pressure against one side of a series of cells containing metallic membranes of palladium alloy. The hydrogen selectively diffuses through the membranes, which completely reject all other gases. The hydrogen recovered from the low pressure side is essentially 100% pure and dry, with less than 1 ppm of total contaminant. The palladium diffusion purifier is a relatively expensive equipment process and is somewhat more costly to operate. In general it has found practical application only where extreme ultrapure hydrogen is an absolute necessity.

Molecular Sieves

Another new means of carbon dioxide removal has been developed which shows great promise as an economical and practical substitute for wet scrubbers. This is a dry process using molecular sieves as a desiccant adsorber.

Figure 1 illustrates a sample of molecular sieve desiccant, a synthetic zeolite material developed commercially about 15 years ago. At that time molecular sieves were something of an answer running around looking for problems. This material was quickly recognized as having a practical application potential for purification processes, particularly in areas of water vapor and carbon dioxide adsorption, for which it has high affinity.

It was necessary for the molecular sieve manufacturers, as well as equipment manufacturers, to make extensive studies of applications and develop practical equipment designs to make its use suitable. In a very short time, molecular sieves became widely used in desiccant dryers for water vapor removal of compressed air and gas streams. Its superior capability compared to conventional desiccants such as activated alumina or silica gel, resulted in economical dryer designs easily able to achieve dew points to levels of minus 100 F.

Many other more specialized chemical and gas process purification applications have been developed since to

FIG. 2. Hydrogen gas generator of 2,000 scfh capacity.

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[1] Presented at the AOCS Meeting, New Orleans, Louisiana, April 1970.

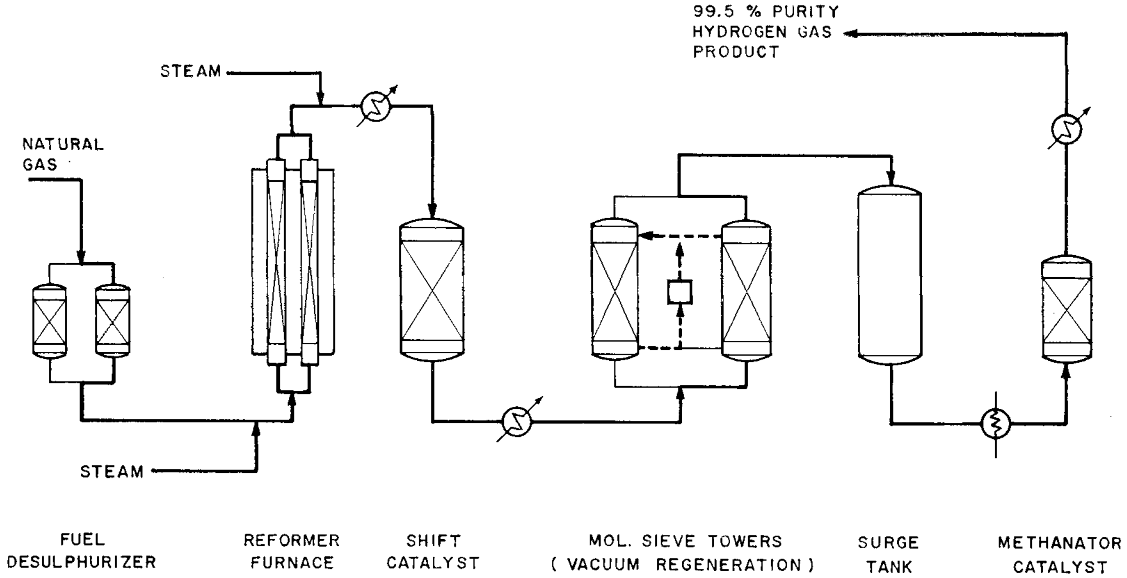

FIG. 3. Molecular sieve type hydrogen gas generator.

take advantage of the unusual properties of molecular sieves. One such example was the development work done in a cooperative project between the sieve manufacturer and surface combustion. About 12 years ago, a bench scale study was instigated to determine the co-adsorption capabilities of CO_2 and water vapor from combustion products (flue gas) of natural gas. The purpose of this work was consideration of possible replacement of the conventional MEA scrubber, refrigerant and desiccant dryer used in the generation of nitrogen atmosphere gas.

Simultaneously, various means of molecular sieve regeneration were also investigated, which included the usual heat regeneration process used in typical desiccant dryers, pressure swing systems from high pressure to atmosphere pressure, pressure swing from high pressure to vacuum, and pressure swing from low pressure to vacuum. Taking into account comparative operating efficiencies and equipment complexities and cost, it became quite evident that the optimum design should employ a dual tower desiccant purifier operating on short cycle regeneration at low pressure which could best be accomplished by vacuum reactivation.

This purifier design produced results comparable to the existing wet processes at comparable equipment operating costs. A full scale molecular sieve type nitrogen generator was then built to complete the studies and confirm the results from bench scale work and refine the commercial equipment design.

This R&D project, which consumed almost three years of work, resulted in a new line of nitrogen gas generators which have been sold commercially since the early 1960's almost to the complete exclusion of the older wet systems.

The typical "package" NX gas generator is capable of producing up to 99% pure, dry nitrogen gas, and is comprised of an exothermic DX gas generator operating at near neutral combustion, a fully automatic dual tower sieve purifier, and mechanical vacuum pump equipment for desiccant regeneration.

TABLE I

Typical Operating Cost Comparisons Per 1,000 SCF

Utility	Rate	Basic system	Optimized system
Natural gas (reaction)	50¢/mcf	$0.140	$0.140
Natural gas (heating)	50¢/mcf	0.123	0.116
Steam (reaction)	75¢/m lb.	0.058	0.055
Steam (regeneration)	75¢/m lb.	0.225	0.113
Cooling water (tower makeup)	6¢/m gal.	0.005	0.005
Electric power	1½¢/kw	0.060	0.015
Cost of utilities per 1,000 scf		$0.611	$0.444

New Hydrogen Purifier

With nearly six years of highly successful results from the molecular sieve purifier for co-adsorption of CO_2 and water vapor, R&D efforts were once again directed to application of this equipment for purification of steam-reformed and shift-converted gas in the production of hydrogen. A year of studies involving modification of equipment sized for this process application resulted in extremely satisfactory performance. Not only do the molecular sieves effectively remove the CO_2 and water vapor, they also demonstrate an ability to partially remove carbon monoxide which may be present in relatively small amounts.

Figure 2 illustrates a recently manufactured "package" hydrogen gas generator of 2,000 scfh capacity. It is comprised of a dual tower activated carbon fuel desulfurizer, a three-tube catalyst reformer, catalyst shift converter, a molecular sieve purifier using a steam jet for vacuum regeneration, and a product gas compressor for delivery at 15 psig. This particular unit is used to supply a protective hydrogen atmosphere in furnace heat treating of jet engine fan blades, hence does not employ methanation catalyst for final cleanup usually required in hydrogenation applications.

With normal reformer methane leakage of 0.1% to 0.2% and residual unreacted CO from the shift converter of 0.1% to 0.2% (approximately 50% of which is removed by the molecular sieves), the final hydrogen present in the fuel gas.

Automatic operation of the molecular sieve towers is accomplished by means of a preset electric cam type cycle timer which controls pneumatically driven automatic switching valve operators.

Figure 3 illustrates a simplified basic schematic flow diagram of a molecular sieve type HX generator for producing hydrogen suitable for oil refining applications. Starting at the left are dual desulfurizing towers of activated carbon for pretreatment of fuel gas, followed by the gas-fired reformer, from which the gas passes through the two-tower molecular sieve purifier, then through

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TABLE II

Typical Product Gas Composition

Gas	From purifier	From methanator
Carbon dioxide	0.05%	0.001%
Carbon monoxide	0.1 %	0.001%
Methane	0.1 %	0.25 %
Dewpoint	−60F	+40F
Hydrogen[a]	99.75%	99.75 %

[a] Includes N_2 present in fuel supply.

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the methanator catalyst converter.

This basic system is best suited to smaller capacity generators where consideration of minimum equipment cost is of greater importance than absolute optimization of overall operating cost. For example, the reformer catalyst tube size and furnace setting is kept at an economical minimum size by the use of slightly higher steam natural gas input ratio. In addition, the system design is kept at its simplest minimum by making no attempt to achieve heat recovery.

Conversely, the operating cost of utility consumption becomes a much more important consideration in larger hydrogen plant designs. Here, research technology is brought to bear in larger size reformer design modifications that permit a change of operating conditions which are able to achieve comparable results with a substantial resultant savings in steam input. This reduced input also is reflected in further savings of heating fuel consumption in the reformer furnace, providing a two-way operating cost reduction.

Further conservation of utilities is also achieved by the use of an indirect heat exchanger to transfer heat in the steam reformed gas to the product gas entering the methanator catalyst chamber, employment of condensate quenching in a two-bed shift converter catalyst tower, and the use of an interstage condenser in the purifier reactivation steam jet vacuum system.

Design Economics

Table I illustrates a typical comparative list of operating costs of the basic system, and the optimized design of molecular sieve hydrogen gas generator, based on average utility rates. To determine justification of the optimized design in comparison with the basic system, a 2,000 scfh unit would produce 16 MM scf per 8,000 hr year operation at an annual utility cost of $9,776.00, as a basic system. Under the same conditions, this same operation as an optimized system would cost $7,104.00 per year, for an annual savings of $2,672.00. Under normal circumstances, this differene in operating cost makes it difficult to consider the added capital expense of an optimized system.

On the other hand, a 20,000 scfh system would produce 160 MM scf/year of hydrogen, which represents a factor of 10 times the operational cost difference. Thus, by considering an annual savings of $26,720.00, the initial added expense of achieving maximum economy of production becomes a very important consideration.

Table II indicates a typical final product gas composition achieved by the molecular sieve type hydrogen gas generator, which includes a methanator catalyst unit for hydrogenation applications. By maintaining methane leakage at approximately 0.1%, and residual unreacted CO at about 0.1%, the dry effluent from the molecular sieve purifier containing less than 500 ppm of CO_2, will result in a methanator treated gas of 99.75% purity, less any nitrogen diluent present in the fuel supply.

While essentially all moisture will be removed from the gas by the molecular sieves, some amount of water vapor will be present in the methanator effluent as a result of the conversion reaction.

Since the molecular sieve purifier design lends itself to the most economical performance at relatively low pressure process operation, it is possible to run the reformer also at greatest economy of heating fuel and reaction steam input to maintain a minimum level of unreacted hydrocarbons.

With the use of a steam jet for molecular sieve vacuum regeneration and, in the smaller generator sizes, the use of high pressure velocity burners on the reformer furnace, there is no electrical power requirement in the operation other than a source of 110 v supply for the control and safety aid circuit.

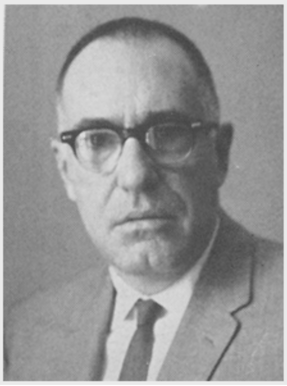
The generator system itself has no blowers, pumps or other motor driven equipment, which would normally be considered maintenance items. (Larger plant designs may employ a combustion air blower for the reformer furnace burner equipment.) A final product gas compressor of the size and type required for specific needs may be added to the outlet of the generator system.

Thus molecular sieves has found proven application for hydrogen production at competitive equipment and operating cost, with comparable purity to more conventional methods of generation from hydrocarbon fuel, while providing simplified, fully automatic operation and substantially greater freedom of potential maintenance.

[Received May 3, 1970]

• *Names in the News . . .*

Peter Kalustian



R. J. Sims

B. L. Thomas Associates, Cincinnati based consulting firm of Edible Fats & Oils experts, announces that Peter Kalustian ('45), has joined their firm. Mr. Kalustian has had over 36 years of experience in foods, and has held many positions of responsibility in production, plant operations, product development, sales and corporate management with the Drew Chemical Corp. He is very well known in the edible fat industry and has had a significant role in the commercial development of hard butters for chocolate-type coatings, special fats for nondairy products, margarines and shortenings. Mr. Kalustian will head the Eastern office of the firm.

R. J. Sims ('50) has been recently promoted to Research Associate at General Foods Corp. Technical Center in White Plains, N.Y. He is now in charge of the Fats and Oils Technology Center of the Corporate Research Department.

C. W. Sampson ('48), General Manager Export Division, Emery Industries Inc. retires after 39 years of service with the company.

R. N. Speer has been elected Vice President-Manufacturing of Universal Oil Products Company. In this new position, Speer, who has been vice president and general manager of UOP's C&H Group, will assume additional line operating responsibilities over certain manufacturing units of the company. In making the announcement, J. O. Logan, president of UOP, said that effective January 1 the divisions of the Transportation Equipment Group will become the responsibility of Speer. General managers of the Aerospace Division, Bostrom Division, Amalga Division and their affiliated units will report directly to Speer.

The Board of Directors of Sandoz-Wander, Inc. has announced the election of A. J. Frey as President and Chief Executive Officer. Dr. Frey, who was formerly Executive Vice President of the Company's Pharmaceutical Division, will serve as Chairman of the Company's Management Committee. Sandoz-Wander, Inc., is headquartered at Hanover, New Jersey.