

## NEW DEVELOPMENTS IN THE GENERATION OF CONTROLLED ATMOSPHERES FOR HIGH TEMPERATURE PROCESSING

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This paper is concerned with recent developments in generating controlled atmospheres from gaseous hydrocarbon fuels by reaction with air. Atmospheres, their generation and control have become a very important consideration in many processes; such as ore beneficiation, metal treating and food and chemical applications. Developments in the generating of hydrogen are excluded, since these have been covered in detail in other papers presented at this symposium.

### I. ADIABATIC (HIGH COMBUSTIBLES) GENERATOR

The increasing use of newly developed or improved ore reduction processes is creating requirements for large quantities of gaseous atmospheres for the reduction of metal oxides. In many cases, such as for copper and iron, a single pure reductant is not required and mixtures of CO and H<sub>2</sub> are suitable, providing the ratios of CO/CO<sub>2</sub> and H<sub>2</sub>/H<sub>2</sub>O are controlled. In these cases, one economical way to prepare such atmospheres in large quantities (100 M - 1 MM cfh) is by means of a fixed bed adiabatic catalytic reactor as shown in flow diagram in Figure 1.

The atmosphere produced consists of CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub> and unreacted CH<sub>4</sub>, and the process may be carried out in several ways depending on the relative concentrations of the oxidizing and reducing agents needed.

Figure 1 incorporates two basic flow schemes, one with a gas preheater and the other without a preheater. No preheat is required if the maximum combustibles content (CO+H<sub>2</sub>) of the product gas is not required to exceed approximately 45%. If the product gas must contain 45 to 60% CO+H<sub>2</sub>, some external energy is necessary to sustain the reaction. This energy is conveniently provided by preheating the gases ahead of the reactor. The product gas leaving the reactor may be discharged at reactor temperature, or superheated to a higher temperature, or it may be cooled. The several options are shown on the flow diagram.

The simplest process is the production of the 45% combustibles atmosphere for use at reactor discharge temperature.

To produce 45% combustibles atmosphere, the catalytic reactor is first brought to approximately 1200°F by passing hot air through the generator. The catalyst is then at a high enough temperature to start the reaction when the reactants are introduced. Heating is accomplished by means of a simple excess air burner and no indirect preheater is required.

After the reactor is hot, reaction air and desulphurized fuel gas are delivered to the generator at suitable pressure, very accurately proportioned and intimately mixed. When this mixture is introduced into the catalytic reactor, typical reforming reactions occur. The exothermic formation of CO<sub>2</sub> occurs near the reactor inlet and the endothermic reactions occur later so that a characteristic temperature gradient persists throughout the catalyst bed. The reactor temperatures rapidly attain equilibrium, and composition of the product atmosphere becomes stabilized quickly so that a constant analysis of product gas is attained within minutes after the reaction is started. In the same manner, the reactor responds rapidly to changes in air-gas ratios to produce the atmosphere desired.

The reactor is shut down by simply closing the gas and air valves and allowing the reactor to cool. Since it is heavily insulated, it will lose temperature slowly and may be restarted without preheating for a number of hours after shutdown. The length of time will depend on the size of the unit and its operating conditions. This is a very desirable feature for applications where gas demands are intermittent.

The production of atmospheres containing greater than 45% combustibles requires the use of a preheater. This is an indirect heater used to heat the reactants during normal operation and to heat the air to bring the reactor to its starting temperature. Other components of the system are identical to the 45% combustibles generator.

The temperature of the product gas leaving the reactor is dependent upon the type of fuel gas used, air-gas ratio and the degree of preheat employed. It has been found that the water gas shift reaction ( $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ ) stays in equilibrium with the discharge gas temperature over a wide range of space velocities. It has also been determined that the unreacted Methane content of the product gas varies in a predictable manner with the discharge gas temperature and the space velocity. Since system heat losses are calculable and small, it is feasible to calculate accurately the air-gas ratio, space velocity, and preheat required to produce a specific analysis of product gas. This in turn permits the rapid attainment of equilibrium conditions after start-up. Figure 2 shows typical reactor operating data, using natural gas or commercial propane fuels with the generator operating at rated capacity. Adjustments can be made to operate anywhere within the limits of Tests 1 and 2 and also under somewhat leaner conditions than shown in Test 1. The relationship between Methane and reactor discharge temperature and space velocity is shown in Figure 3.

Major development considerations center around the proper design of the reactor catalyst bed, means for introducing the reactants into the bed, and the selection of suitable catalyst to make the process operate without exceeding the temperature it limits and without carbon deposition. The equipment which has been developed successfully meets the application requirements.

Approximate equipment and utilities costs for typical adiabatic reactors are shown on Figure 4. Equipment costs include air compressor and adequate instrumentation. Utilities are based on natural gas at 50¢/M scf, and electric power at 3/4¢/KWH. Product gas is at one atmosphere pressure and reactor temperature. A photograph of a high combustibles adiabatic reactor is shown in Figure 5.

## II. NITROGEN GENERATOR

Nitrogen generators are widely used throughout industry for purging, blanketing, heat treating, and many other operations requiring so called inert atmospheres to insure safe operation and/or improved processing. The nitrogen for such applications can be provided by many methods. Small demands are satisfied by using cylinder gas; larger requirements by on-site production via a variety of methods. One inexpensive means is by removing  $\text{CO}_2$  and  $\text{H}_2\text{O}$  from the products of combustion of hydrocarbon fuels. The nitrogen produced contains small concentrations of CO and  $\text{H}_2$  which are generally controlled between 0.5% and 4.0%, making the nitrogen sufficiently pure for the majority of applications.

At the present time numerous purification systems and generators have been developed and are being used for this purpose. The majority of such generators use an adsorption system to remove  $\text{CO}_2$  and refrigeration and/or adsorption systems for dehydration. Typically the  $\text{CO}_2$  absorption system is a closed Monoethanolamine (MEA) solution which absorbs  $\text{CO}_2$  from the process gas and in turn is regenerated by utilizing the exothermic heat of combustion released in the preparation of the process gas. The adsorption dryers are normally of the thermally reactivated alumina type. These generators are highly developed, reliable and efficient machines, but are subject to corrosion problems. Over the years, considerable work has been done to circumvent this problem by many means, especially using dry adsorbent systems to remove both  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . This developmental activity has increased with the advent of higher

capacity adsorbents such as the Molecular Sieves.

Many systems have been devised to apply these new adsorbents to the manufacture of simple, reliable, and economical nitrogen gas generators. One method is shown diagrammatically in Figure 6. Operation is generally as follows:

Air and fuel gas are proportioned by suitable flow rationing means and burned in an exothermic gas generator wherein the products of combustion are cooled either directly or indirectly with cooling water. The cooled gas contains nitrogen, generally with approximately 11% CO<sub>2</sub> and 1.0 to 4.0% combustibles. It is saturated with water at approximately cooling water temperature. The cooled gas enters the right hand adsorbing bed at a pressure slightly above one atmosphere. Both CO<sub>2</sub> and H<sub>2</sub>O are adsorbed from the gas stream by the adsorbent in the tower, and thus<sup>2</sup> dry nitrogen containing essentially 1/2% to 2% CO and 1/2% to 2% H<sub>2</sub> is produced.

While the right hand bed is purifying the process gas stream, the left hand bed is being reactivated. This is accomplished without heat by maintaining the desorbing bed under a vacuum during the desorption cycle and utilizing some of the product nitrogen as a purge gas to sweep the desorbed CO<sub>2</sub> and H<sub>2</sub>O from the reactivating bed. Re-activation is accomplished without additional heat<sup>2</sup> and at essentially ambient temperature. After reactivation the left tower is repressurized. The towers are cycled alternately so that one is adsorbing CO and H<sub>2</sub>O at all times, and the other desorbing or reactivating. A continuous flow of nitrogen<sup>2</sup> is maintained from the system.

Cycle times are less than 10 minutes to maintain essentially adiabatic conditions in the towers and to minimize the quantity of dessicant required. Cycle time is determined by the economics of nitrogen loss for purging and repressurizing, and pump down desorption times.

The pressure swing system is automatic, simple, and has few components. Equipment costs are comparable to MEA systems and utility costs are approximately 13¢ per MCF nitrogen.

Figure 7 is a photograph of a nitrogen generator of the type described.

### III. EXOTHERMIC GAS GENERATORS

Because of their simplicity and economy, exothermic generators continue to be used for processes and in applications in which nitrogen containing CO<sub>2</sub> and H<sub>2</sub>O in relatively high concentrations and CO, CH<sub>4</sub> in small concentrations are not detrimental. Many heat treating processes in ferrous and non-ferrous metallurgy utilize exothermic generator atmospheres. For example, the annealing of sheet steel, aluminum sheet, coils and foil, copper alloy and also the calcining of charcoal, all represent uses of such atmospheres for high temperature processes. At lower temperatures exothermic generator atmospheres are used in grain storage and for safety applications. Figure 8 shows the compositions of several typical atmospheres which may be produced from exothermic generators. In many cases the generators are expected to operate over the entire range of air-gas ratios shown and they must be designed accordingly.

The simplicity of exothermic gas generating equipment may be seen in Figure 9. The air-gas proportioning system is identical to that used for the nitrogen generator.

Since the main attribute of this type of atmosphere is its low equipment cost and operating economy, emphasis has been and is on producing more gas in a single generator and at the same time decreasing the physical dimensions of generators.

The air-gas mixing and burner system is probably the major consideration in the designing of exothermic generators. Poor mixing will result in stratification of the

gases and non-uniform and incomplete combustion. Slightly rich or lean zones will develop at the mixer and burner and will persist throughout the combustion chamber. This will result in the production of exothermic gas containing some free oxygen in a rich gas atmosphere or some combustibles in a lean gas atmosphere. This problem becomes more difficult as generator capacities increase.

An ideal mixer and burner system will intimately mix and allow the air and fuel gas streams to react in as short a time as possible in order to keep pre-mix and combustion volumes at a minimum. From a safety standpoint a nozzle mixing system is desirable since it eliminates hazardous pre-mix volumes altogether and does not require fire checks. For large capacity generators this is especially desirable, since otherwise multiple fire check and burners are required, both of which increase the cost and operating complexity of the equipment.

The problem of developing a simple nozzle mixing burner system for large generators is difficult and becomes more so as generators increase in capacity. This is because of the longer mixing paths associated with larger equipment.

Many approaches to the problem have been used and much development work has been done. Hydraulic studies, cold gaseous models using various tracer techniques and special hot probe studies have been employed to evaluate the characteristics of various mixing and burner systems. As a result of such work, large nozzle mixing burners have been developed which mix well with a minimum expenditure of energy and promote complete combustion in a small volume. Figure 1 shows one such generator, 120,000 scfh capacity, using a single nozzle mixing burner. Development is continuing to insure improved performance as the demand for generators of increasing capacities continues.

The generator shown in Figure 10 also incorporates a gas cooling system which is an integral part of the unit. The purpose is, again, simplicity and saving of floor space. The cooler consists of an annular shaped packed tower surrounding the combustion chamber. Gas is passed upward through the cooler and is cooled by water flowing downward. Where it is necessary to employ indirect cooling, condensate from the products of combustion is cooled and recirculated through the cooler. This is one of several compact cooling systems which are being used successfully on exothermic generators at the present time.

The general trend of virtually all classes of generators is towards more accurate control of product gas composition, increasing emphasis on automatic and simplified operation, and the production of increasing quantities of gases in smaller floor spaces at a lower capital expenditure. Continually improving instrumentation for analysis and control and the development of analytical techniques aided by computers is permitting a better understanding of the important mechanisms of gas generator systems and the development of improved equipment to meet industrial demands. The development of the three generators described in this paper are a direct result of the modern technological advances of the last few years.

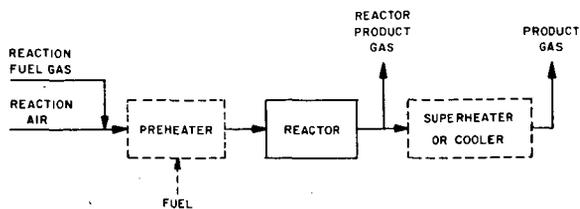
ADIABATIC CATALYTIC REACTOR FLOW SCHEME

FIGURE 1

ADIABATIC REACTOR OPERATING DATA

	<u>TEST-1</u>	<u>TEST-2</u>	<u>TEST-3</u>
AIR/GAS RATIO	3.43	2.49	7.04
REACTANT PREHEAT	NO	YES	YES
MAXIMUM BED TEMPERATURE °F.	1970	1700	2000
PRODUCT TEMPERATURE °F.	1500	1550	1720
PRODUCT ANALYSIS - %			
CO <sub>2</sub>	2.7	0.25	0.3
CO	16.0	20.1	23.7
H <sub>2</sub>	28.9	38.3	30.6
CH <sub>4</sub>	0.9	0.5	0.3
N <sub>2</sub>	51.5	40.3	44.6
H <sub>2</sub> O	-	0.55	0.5

FUEL: TESTS 1 AND 2 - TOLEDO NATURAL GAS  
 TEST 3 - COMMERCIAL PROPANE

OPERATING PRESSURE - 1 ATMOSPHERE

FIGURE 2

EFFECT OF SPACE VELOCITY & TEMPERATURE  
ON RESIDUAL METHANE

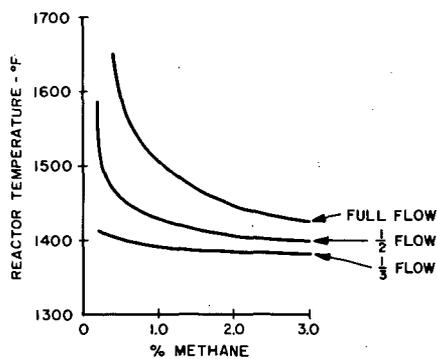


FIGURE 3

ADIABATIC REACTOR  
EQUIPMENT AND UTILITY COSTS

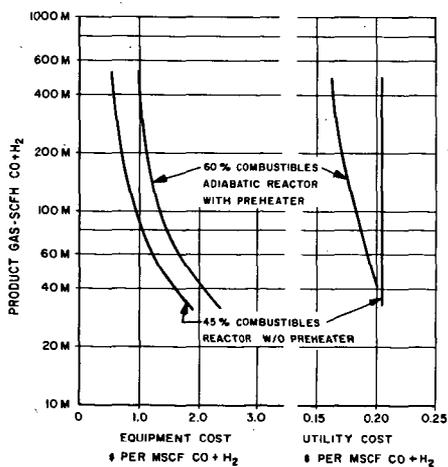
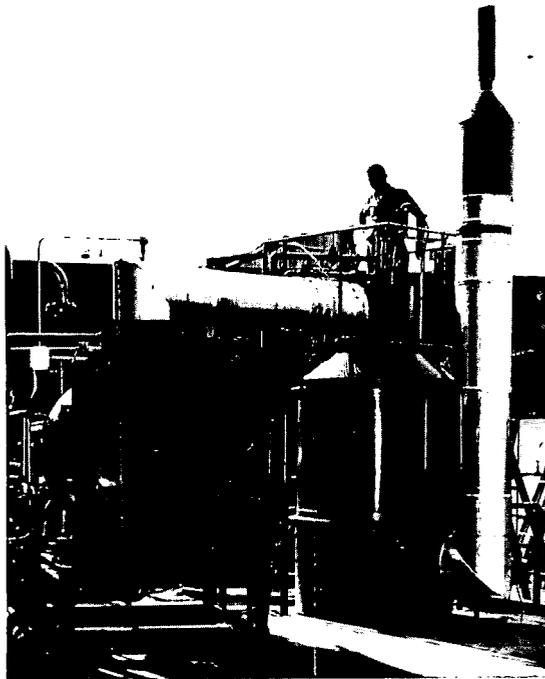


FIGURE 4



ADIABATIC REACTOR  
FIGURE 5

NITROGEN GENERATOR FLOW SCHEME

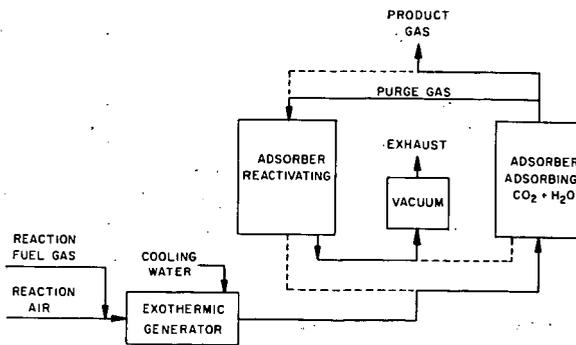
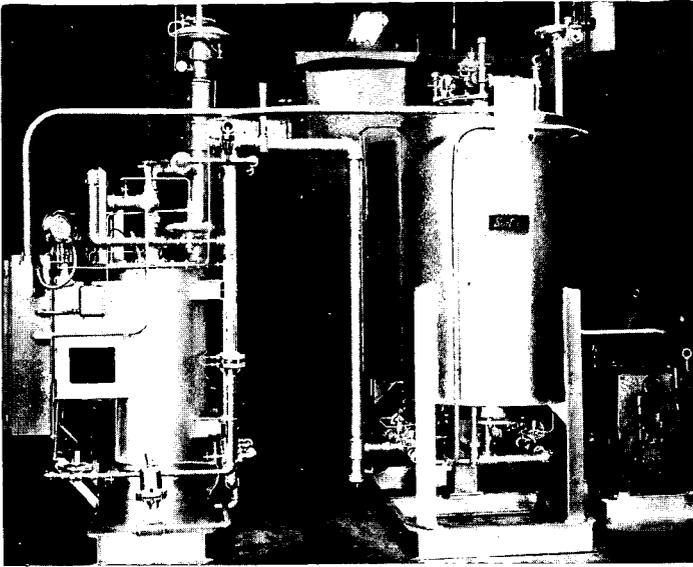


FIGURE 6



NITROGEN GENERATOR  
FIGURE 7

EXOTHERMIC GAS GENERATOR  
TYPICAL GAS COMPOSITIONS

AIR/GAS RATIO	6.2	9.0	10.0
DRY ANALYSIS - MOL %			
CO <sub>2</sub>	5.3	11.0	11.0
CO	9.8	1.3	0.0
H <sub>2</sub>	10.4	0.7	0.0
CH <sub>4</sub>	0.1	0.0	0.0
O <sub>2</sub>	0.0	0.0	1.3
NO	0.0	0.0	0.1

BASIS: TOLEDO NATURAL GAS, PRODUCTS AT ONE ATM.

FIGURE 8

EXOTHERMIC GAS GENERATOR FLOW SCHEME

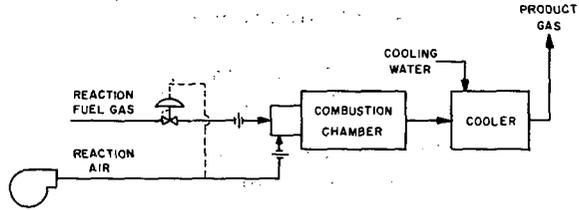


FIGURE 9

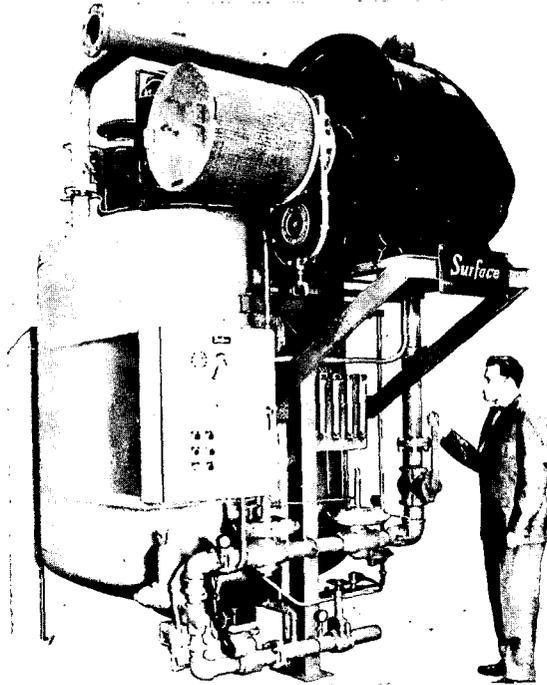


FIGURE 10