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THERMAL FIXATION OF ATMOSPHERIC NITROGEN

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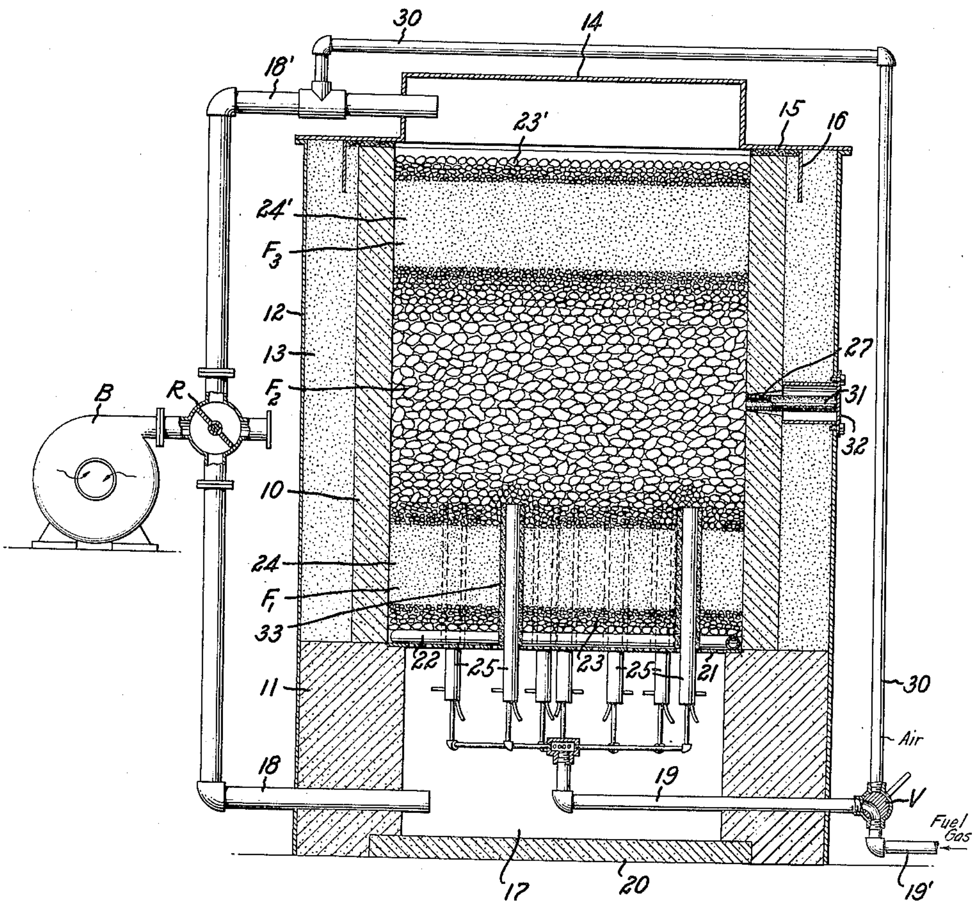

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THERMAL FIXATION OF ATMOSPHERIC NITROGEN

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Application June 6, 1944, Serial No. 538,898

4 Claims. (Cl. 23—163)

This invention relates to the high temperature treatment of gases. It is particularly concerned with improvements in the process of, and apparatus for, thermally fixing atmospheric nitrogen as nitric oxide.

It heretofore has been suggested (U. S. Patent No. 777,485 to Pauling) that nitrogen dioxide might be produced by passing air through a series of highly heated checkerbrick stoves and thence through a series of relatively cold checkerbrick stoves. For implementing such a process, patentee proposed that the two series of checkerbrick stoves be arranged at the two ends of an electric arc furnace employing carbon electrodes, and that the process be divided into two steps, as follows: In the first or heating step, the heat from a plurality of electric arcs (located in the electric furnace) was to be transferred, by means of a current of air or other suitable gas, to the checkerbrick stoves, there being used a sufficient number of passes of the heat-carrying gas to bring the temperature of the parts of the stove nearest the electric furnace and approximately to the temperature of the latter, whereupon the electric current was to be interrupted and the electrodes withdrawn. In the second or nitrogen-fixing step, air was to be passed through the succession of stoves (and non-functioning electric furnace) in alternate direction, for a number of passes and until the necessary high temperature for nitrogen fixation no longer existed in the stoves, whereupon step two was to be discontinued and step one resumed.

This suggested process (and apparatus) was not technologically feasible for a number of reasons of which only two need here be mentioned, the same being: (1) the slow rate of cooling (of the highly heated air) by the checkerbrick stoves is out of all proportion to the rapid rate of dissociation of nitrogen oxide at or near the maximum temperature (2500° C. or 2700° C.) of Pauling's process, from which circumstance it results that no substantial amount of desired product can be recovered; and (2) the successive periods of heating and of nitrogen-fixing suggested by Pauling are altogether too long, since it is a fact that great variations in the extent of nitrogen fixation attend substantial variations in the "top" temperature being employed.

More recently, the thermal fixation of atmospheric nitrogen as nitric oxide has been successfully practiced in an improved process which involves the use of a pair of "pebble beds" of refractory particles of relatively small size, with an enclosed combustion space communicating between them. The functionally central combustion space may be empty (i. e., devoid of filling material), or it may be constituted by a space filled with refractory chunks of relatively large size. The so-characterized apparatus may be in the form of two vertically disposed, heat-insulated, pebble-bed stoves with a horizontal, heat-insulated cross-over communicating between their top portions (which cross-over might be empty or might be filled with large refractory lumps), or (as is disclosed in application Serial No. 498,896, filed August 16, 1943, by William G. Hendrickson and Frank M. Wolf jointly with the present applicant, now Patent No. 2,421,744) it may be a "vertical silo" type of furnace including a vertical tubular wall of refractory material enclosing a gas-traversable shaft filling consisting essentially of two pebble beds, each formed of relatively small refractory particles, one above the other and separated by a relatively thick (tall) column or bed of larger sized refractory bodies. The "relatively small refractory particles" may vary in size from that of coarse sand (i. e., through 14 on 18 mesh Tyler screen) through the sizes of smaller and larger gravels up to those of generally rounded small rocks equivalent in mass to spheres of 2'' diameter. The "larger sized refractory bodies" may be chunks of refractory material several inches (e. g., more than 2 inches and up to 5 or 6 inches) in average diameter. The amount of voids varies, but generally lies between about 35% and 40% of the over-all volume of the assemblage. Illustrative of the surface area-volume relationship above referred to are the following data of surface areas, in square feet, of 1 cubic foot assemblages of differently sized refractory bodies of spherical shape, with 40% of void space:

Table

Average diameter		Mesh size opening (Tyler)	Total surface area, in sq. ft. per 1 cu. foot
Inches	Feet		
2.	0.166	----------	21.6
1.67	0.139	----------	25.9
1.	0.0834	----------	43.2
0.5	0.0417	----------	86.4
0.2	0.0167	3–4	216
0.125	0.0104	6	334
0.1	0.0083	7–8	432
0.0625	0.0052	10	720
0.005	0.0026	12–14	864

In the processes associated with both the types of thermal fixation furnaces generally described above, a "heat plug" of very high temperature heat is to be established within one or the other of the two pebble beds, and air is to be forced into the outer end of, and through, the heated pebble bed, through the functionally central combustion space and into and through the relatively cold pebble bed, the rate of flow of the air and the size of the particles constituting the two pebble beds being so adjusted that in its passage through the apparatus the air is heated to a temperature at which nitrogen and oxygen react to form NO and then is cooled, to a temperature at which the rate of decomposition of NO is so slow as to be negligible, at an extremely rapid rate of cooling. When the "heat plug" has been transferred from the first to the second pebble bed (one-half of the complete cycle), the direction of the air stream is reversed and the procedure is repeated to complete the second one-half of the cycle. Concurrently, fluid (e. g., gaseous) fuel is introduced into the pre-heated air passing through the combustion space, and in the same direction as that of the air, in amount sufficient, by its combustion, to insure maintenance of the necessary high temperature for the nitrogen-oxygen reaction. For that purpose, each of the two types of fixation furnace includes a plurality of fluid fuel inlets, at least one at either end of said combustion space.

In the furnace structure described and claimed in the previously noted application Serial No. 498,896 said fluid fuel inlets are projected inwardly from the cold ends of the pebble beds through or partially through the latter toward the centrally disposed column of relatively large refractory "chunks" or bodies. The fuel (which may be hydrogen or an industrial gas relatively rich in hydrogen, carbon monoxide, water gas, producer gas, coke-oven gas, gaseous hydrocarbons such as methane, natural gas, or the like) is fed into the combustion space during the full cycle, i. e., during both the "upstroke" and the downstroke.

It has been found that the above-described procedure (as carried out in either of the above two types of furnace) may be improved as to yield and as to economy; that the construction of the apparatus may be simplified and cheapened, and that the maintenance and operation of the apparatus may be improved, by dispensing with the fuel inlet device or devices located at one end or the other of the centrally located combustion space and by adding fuel during one-half, only, of each complete cycle. In the case of the "vertical silo" type furnace, it has been found advantageous to retain the bottom fuel inlet device or devices and to eliminate the one or ones located at the top, and to add the amount of fuel necessary for maintenance of the required high temperature during the upstroke, only, of the cycle. By so doing, it surprisingly results that even though heating is being effected for only one-half of the time while cooling occurs during the other one-half of the time, these alternating conditions are of such relatively short duration (one-half cycle each) that the attendant variations in "top" temperature may be so negligibly small as not materially to affect the conditions of the N_2+O_2 reaction. It has been found that these relatively very brief but frequent additions of heat of high intensity to the system during one-half of each complete cycle do not work the disadvantages inherent in the two-step process of Pauling.

This improvement brings about a number of

desirable results. Dispensing with fuel inlet devices at the top of the vertical type furnace avoids complications incident to fuel and water connections at that part of the furnace and materially simplifies the construction and maintenance of the apparatus. Moreover, by so doing, the heat losses through water-cooled fuel inlet devices are cut in half, thereby effecting some saving in fuel cost. Burning fuel during the upstroke half of the cycle is more satisfactory than burning it during the downstroke—especially in case a fuel gas rich in thermally unstable constituents (e. g., hydrocarbon gases) is being employed. Probably the most important advantage is that by eliminating fuel inlet devices from the top of the vertical silo-type furnace the difficulties incident to displacement of such devices, brought about by the seemingly inevitable settling of the pebble beds during the "break-in" or initial period of operation of the furnace, are avoided.

Additional advantages which may result from the improved process include the following: It may, in certain instances, be highly desirable to avoid contaminating the nitric oxide recovery system with water vapor or/and carbon dioxide: in such event, I can divert the upstroke gases from the principal nitric oxide recovery system and cause to pass to the latter only those gaseous products which result from the downstroke halves of the cycles, and may if desired supplement this measure by drying the atmospheric air used for the fixation. The so diverted gases can be separately processed for their content of nitric oxide or for their content of residual heat, or they may be wasted. In other instances, it may be advantageous to divert the upstroke gases and waste or otherwise process the same, in order to take advantage of the circumstance that the downstroke gases may possess a larger content of nitric oxide by reason of the higher concentration of oxygen for fixation with nitrogen obtaining when combustion is not occurring.

The equilibrium for the reaction $N_2+O_2=2NO$ is

$$K=\frac{C^2_{NO}}{C_{N_2}C_{O_2}}$$

and it is clear that the concentration of nitric oxide obtainable at equilibrium increases directly as the square root of the oxygen concentration

$$C_{NO}=\sqrt{KC_{N_2}}\sqrt{C_{O_2}}$$

For example, at a temperature of 2127° C. the equilibrium concentration of NO is 2.0% in air which contains 20% oxygen; when half of the oxygen has been consumed (as by combustion) leaving only 10% of oxygen in the mixture, the equilibrium concentration of NO is reduced to 1.4%, and with 5% oxygen it is reduced to only 1.0%.

However, in operating a large sized NO furnace I have found that oxygen concentration is not widely different in the two strokes, and hence for usual purposes it is desirable to recover NO from both halves of the cycle.

Instead of positively wasting the upstroke gases, in cases where I do prefer to divert the latter, I may employ two independent nitric oxide recovery systems (dissimilar or similar) to one of which the downstroke gases are passed and to the other of which the upstroke gases are passed.

The concept of the present invention is not restricted to embodiment in the vertical silo type of furnace, even though the advantages are more numerous in connection with the latter than they are in connection with an apparatus comprising two vertical stoves connected by a cross-over. The particular design of the nitric oxide furnace is not a limiting factor, and the improved process of the present invention is operable whether the fuel is introduced from an end of the shaft filling or whether it is introduced through the side wall of the furnace directly into the combustion space. Moreover, the improved process is operable whatever may be the construction of the shaft filling—i. e., whether they be beds of true pebbles or bedded assemblages of relatively small refractory objects having shapes other than that of a pebble, provided that the bed thereof, when assembled by an ordinary mode of assembly, is characterized by a substantial amount of voids or interstices (generally 35% to 40% of the over-all volume of the bed) providing therethrough a multitude of fluid channels of small mean hydraulic radius. In this connection it is to be noted that the composition of the pebbles (or functional equivalents of pebbles) should be such that the refractory objects do not fuse or vaporize or volatilize at the maximum temperature of operation (e. g., from about 2000° C. as a minimum to about 2400° C.): selection is practically restricted to periclase, dead burned magnesite, dead burned lime, zirconia, fused magnesia and similarly high-fusing oxides.

The invention will now be described in greater detail, and with reference to the accompanying drawing, in which the single figure is an axial vertical sectional view of a preferred embodiment of apparatus in accordance with the invention.

In the figure, F1, F2, F3 taken together represent a shaft filling in a "vertical silo" type furnace; it is enclosed within a cylindrical refractory wall 10 of rammed magnesia supported upon a base 11 of heat-resistant concrete (lumnite) or equivalent construction material. 12 represents an outer metal (e. g., sheet iron) shell surrounding wall 10, and 13 is a mass of loose unclassified magnesia insulation supported by base 11 and filling the annular space between wall 10 and outer shell 12. Said annular space is made substantially gastight by means of a centrally domed cover 14 which is secured, along its periphery, to outer shell 12 and which makes a substantially gas-tight fit against the top of wall 10 by interposition therebetween of a caulking layer 15 comprising a suitable "mortar" or paste of finely divided magnesia backed by asbestos packing. As is indicated in the drawing, a depending baffle ring 16 may be secured to the underside of cover 14 along an annulus concentric with but spaced from wall 10, and the asbestos packing of caulking layer 15 may, as shown, be extended outwardly from wall 10 under cover 14 to such baffle ring. A function of this baffle ring is to deflect any gas, seeping from the furnace, downwardly into the mass 13 of loose insulation.

The lumnite base 11, of substantial depth, is formed to provide a base chamber 17 substantially concentric with but of smaller diameter than wall 10, into which base chamber there project, through said base, a conduit 18 for introduction of air under pressure and a second conduit 19 for fuel gas. As is diagrammatically illustrated in the drawing, a portion 20 of the base 11 may be so cast as to be removable from the base whereby to provide access to base chamber 17.

The top opening of base cavity 17 is bridged by a plurality of spaced metal bars 21. These latter may constitute the grate for the shaft filling, or they may serve to support a water-cooled grate 22. This latter comprises a coiled iron pipe whose inlet and outlet connections (not shown) pass through base chamber 17 and base 11 to the outside. Upon bars 21 or grate 22 is supported the shaft filling F1, F2, F3.

Zone F1 of the shaft filling is composed of (*a*) a relatively thin layer 23 of macadamized refractory pebbles in sizes ranging upwardly from 1 inch diameter pebbles immediately adjacent grate 22 to ¼–½ inch diameter pebbles and (*b*) a superposed pebble bed 24 of refractory pebbles of one-fourth to three-eighths inch diameter. It is noted, at this point, that the main function of macadam 23 is to support pebble bed 24 and to maintain the same against sifting through grate 22. Were grate 22 so constructed as to be able directly to support pebbles of the relatively small pebble bed 24, macadam 23 might be omitted.

Adjacent to and above that portion of the filling which constitutes zone F1 is a column of symmetrically doubly macadamized refractory bodies constituting zone F2 of the shaft filling. As will be clearly understood from an inspection of the drawing, the symmetrical double macadamization is brought about by superposing over pebble bed 24 a succession of layers of larger and larger pebbles ranging from 4–6 mesh, immediately adjacent the top of pebble bed 24, through ¼–½ inch, ½–¾ inch, 1 inch, 2 inch and 3 inch sizes to a central mass of 5 inch chunks of magnesia, and an upper reverse succession of the layers to a top layer of the 4–6 mesh pebbles. The thicknesses of the several layers of refractory bodies in portion F2 vary between say 1 inch for the layers of 4–6 mesh material to say 6 inches for the layers of 3 inch material and 6 inches for the 5 inch chunks. That portion of the filling which is constituted by an assemblage of refractory bodies having an average diameter in excess of 2 inches presents materially less than 22 sq. ft. of surface area per 1 cu. ft. of volume thereof, whereas those portions which are constituted by assemblages of refractory bodies or particles having an average diameter of less than 2 inches present less than 22 sq. ft. of surface area per 1 cu. ft. of volume.

Zone F3 of the shaft filling is constituted by a bed 24′ of 6–10 mesh material, identical with bed 24, above and immediately adjacent to top of portion F2, and a top macadam 23′ identical with bottom macadam 23 except that the direction of macadamization is here reversed.

Into the dome space of cover 14 there leads an air conduit 18′, similar to conduit 18 at bottom space 17.

A plurality of water-jacketed fuel gas inlets 25, 25 are located in the lower portion of the furnace. These devices communicate, by means of branch fuel pipes as shown, with fuel gas conduit 19. Each of devices 25 extends inwardly (i. e., upwardly) from space 17 through the grate 21 (or, 21—22) and into and through zone F1 of the shaft filling, and may, as shown, project a few inches into the lower macadam of zone F2. The upper, open ends of devices 25 may, as shown, be surrounded by mounds of loose pebbles of sizes too large to drop into the mouths of the fuel gas inlets: in lieu of such mounds of larger pebbles there may be used unitary, gas-permeable "caps" of fritted or incipiently sintered pebbles or equivalent refractory materials. Those portions of devices **25, 25** which are subjected to high temperature may, as shown, be provided with heat-insulating coverings or sheaths **33, 33**; these latter may be tubes of rammed magnesia or other suitable material.

If desired there may be provided in wall **10** an outwardly tapered opening **27** for the reception of a refractory tube **31** which at its inner end fits the tapered opening: this tube bridges the space between wall **10** and the outer shell **12**, and may and preferably does extend radially outwardly from the latter a matter of several inches. The tube is provided with a movable closure **32**. Tube **31** serves for introduction of a pyrometer (e. g., optical pyrometer) or other instrument for determining a condition (e. g., temperature) occurring within the shaft filling or/and for use in the initial ignition of a fuel gas-air mixture. In connection with this latter function, it may be remarked that such initial ignition may be effected also by use of known suitable electrical means, e. g., a sparking device, positioned in portion F2.

Fuel gas conduit **19** is provided with a multiway valve V giving access, as desired, either (by means of conduit **19'**) to a source of fuel gas under pressure (not shown) or (by means of conduit **30**) to a source of air under pressure; this latter conveniently may be conduit **18'**.

The blowing equipment B for supplying air under pressure through conduits **18** and **18'** successively, the reversing mechanism R for periodically reversing the direction of the air current, and the valve mechanism V for opening and closing fuel gas conduit **19** and for closing and opening air conduit **30** synchronously with changes in the direction of the air current appear diagrammatically in the drawing as indicating such standard means as may be appropriate for the purpose.

The operation of the above-described apparatus will now be described. Starting with the apparatus "cold," I heat the zone F2 and one of the zones F1 and F3 of the shaft filling to nitrogen-fixing temperature as follows: A current of air is forced through the shaft filling in one direction—say, from the bottom—under sufficient pressure to give a current of, say about 250 cu. ft. over minute per sq. ft. of cross-sectional area of the pebble bed, and simultaneously a stream of fuel gas is introduced into the filling at zone F2. The fuel gas and air mix in the interstices between the relatively large pebbles or chunks of said zone, and combustion of the mixture is initiated at this point. The hot products of combustion move through the remainder of zone F2 and into and through the "far" pebble bed (here, zone F3), giving up their heat to the same and passing out of the filling at substantially room temperature.

When the "far" pebble bed has been heated (as evidenced by a rise in the temperature of the effluent gas), the air current reversing mechanism is actuated and simultaneously passage of fuel gas into the "near" pebble bed is stopped. The incoming air becomes heated by heat-exchange with the heated pebbles of zone F3 in passing therethrough, transfers the heat to the pebbles of zone F1, and passes out of the latter at substantially room temperature, thereby completing one cycle.

This cycle of operations is repeated with gradually increasing combustion temperatures until the desired nitrogen-fixing temperature has been reached, whereupon in the continued operation the relative amount of fuel gas being introduced is adjusted to that amount necessary (by its combustion) to maintain said desired temperature in zone F2. At said temperature and in said zone an amount of nitrogen of the air enters into an endothermic reaction with a chemical equivalent of uncombined oxygen of the air to form nitric oxide, which latter, admixed with residual air and with gaseous combustion products, in passing through the "far" pebble bed is quickly cooled to a temperature at which nitric oxide is stable and eventually to a temperature substantially equal to that of the air entering the near pebble bed.

The gas effluent from the system during the "upstroke" half of the complete cycle may be led to suitable apparatus (not shown) for recovering nitric oxide therefrom; or, if so desired, it may be wasted to atmosphere or otherwise disposed of.

During the "downstroke" half of the cycle (i. e., blowing from conduit **18'** downwardly through the shaft filling to space **17**) the high-temperature heat plug initially resident in zone F3 is transferred to zone F1 of the shaft filling without admixture of fuel gas with the air; hence, during this half of the cycle the air is not contaminated with combustion products and its oxygen content is not depleted by combustion but rather is available for the $N_2+O_2=2NO$ reaction. Wherefore, a somewhat greater amount of nitric oxide is produced during said downstroke than during the upstroke. The gaseous products resulting from the downstroke are led to suitable apparatus (not shown) for the recovery of nitric oxide therefrom.

By means of conduit **30** and multiway valve V I can, when desired inject relatively small streams of relatively cool air under pressure, from air conduit **18'**, through conduit **19** and fuel gas-injecting devices **25, 25**, into the lower "edge" of the median zone F2 of the sheet filling during say an initial part (or even all) of the "downstroke" half of the cycle during which half of the cycle injection of fluid fuel through conduit **19** and devices **25, 25** is interrupted. The so-injected air, which is moved downwardly through zone F1 by and ahead of the "heat-plug" simultaneously being moved downwardly through the shaft filling from F3 toward and to F1 during said "downstroke" half of the cycle, serves to chill the pebbles of zone F1 which are adjacent zone F2, and hence to enhance the chilling effect executed by the pebbles of zone F1 upon the downstroke current of NO-containing air moving from F2 into F1.

It is advantageous, usually, from the standpoint of the subsequent recovery of oxides of nitrogen from the gaseous reaction products, to minimize the amount of water vapor in the latter. The above-described "half-cycle heating" procedure tends to minimize the moisture content of the gaseous reaction product produced during the interval (e. g. during the "downstroke" half of the cycle) when fluid fuel is not being introduced into and burned in the combustion space. A further reduction in the moisture content of the product produced during the "downstroke" is effected by relatively thoroughly dehydrating the atmospheric air being passed through the furnace during this half cycle. Thereby the oxides of nitrogen-containing gaseous product, produced during the "downstroke" interval, is made relatively free from the moisture normally occurring in atmospheric air and, as well, free from water produced by combustion of hydrogen and hydrocarbonaceous gases of the fuel.

While substantially anhydrous air for this purpose can be produced by any known means, one specific embodiment of the present invention consists in using for the "raw material" being passed through the furnace during the downstroke interval air which has been dehydrated by passage through a bed or body or shower of hot dry solid adsorbent particles (e. g., hot dry silica gel particles) maintained at such temperature, and otherwise so adapted, as to remove substantially all of the naturally occurring water vapor from the air. This drying step may be and preferably is a step in the cyclical process, invented by me and described and claimed in my application Serial No. 501,577, filed September 8, 1943, now abandoned, for recovering oxides of nitrogen from the gaseous reaction product containing the same by means of solid adsorbents (e. g., silica gel). In this event, the suction side of blower B is provided with a branched valved conduit one valved branch of which may be used in drawing normal atmospheric air into the NO furnace system and the other valved branch of which is connected to such recovery system and may be used for drawing dehydrated air into the NO furnace system. Thus, I may operate two NO furnaces by the "half-cycle heating" principle, so arranged that one of them is on upstroke while the other is on downstroke, and divert first to the one and then to the other of this pair of furnaces dry air from the oxides of the nitrogen recovery system. Said "dry air" may, for example, be the gaseous reaction product (from a previous cycle) denuded of oxides of nitrogen.

It is desirable that the fuel inlet devices **25**, **25** be provided, along those portions thereof which contact the pebbles of the shaft filling, with the heat-insulating sheaths **33**, **33**. These minimize the amount of heat lost to the circulating water in the water jackets of the fuel inlet devices and therefore save fuel. Moreover, they are desirable in order to avoid the possibility that "short-circuiting" of the air stream occurs during the upstroke half of the cycle. Thus, were the devices not so insulated their cold surfaces would tend to cool profoundly adjacent portions of the pebble bed and hence to keep the air in those portions cold; with the great difference in volumes of the air at say 300° C. and at 2400° absolute, an inordinate proportion of the total air blown would move through the colder zones adjacent the unprotected devices.

It is to be understood that considerable latitude exists as to the sizes of the pebbles constituting the preheating and quenching beds. Thus, the pebble size may range between a size through 6 and on 10 mesh Tyler screen and 1 inch, or more, in diameter. There is similar latitude as to the size of the refractory objects constituting the intermediate bed in which combustion is to be effected. It is to be understood also, that the tubular wall **10** may be formed from suitable refractory brick instead of from rammed magnesia.

The furnace structure of the present invention has, as was stated hereinbefore, utility not only in connection with the thermal fixation of atmospheric nitrogen as nitric oxide but also in connection with the carrying out of other processes wherein gases or vapors are to be reacted or treated under high temperature conditions. Thus, the furnace is adapted for use in partial oxidations of gaseous or readily vaporizable organic materials in situations wherein it is desired to carry the oxidation to a desired stage and thereat to stop the "oxidation" reaction by quickly "quenching" the gaseous reaction mixture. The furnace also is adapted for use in the thermal reformation of gaseous hydrocarbons.

I claim:

1. In a process for the thermal fixation of nitrogen as nitric oxide, the steps which comprise: passing a gas containing nitrogen and oxygen in alternate upward and downward runs through successive beds of refractory bodies in a shaft furnace, said beds comprising an intermediate bed of relatively large bodies and upper and lower adjacent beds of relatively smaller bodies, and heating said intermediate bed to a high temperature sufficient to induce the oxidation of nitrogen by injection of a fluid combustible adjacent the junction of said intermediate bed and that bed of relatively smaller bodies which is first contacted with said gas containing nitrogen and oxygen during at least a portion of each run in one only of said directions, and recovering nitric oxide thus produced.

2. In a process for the thermal fixation of nitrogen as nitric oxide, the steps which comprise: passing a gas containing nitrogen and oxygen in alternate upward and downward runs through successive beds of refractory bodies in a shaft furnace, said beds comprising an intermediate bed of relatively large bodies and upper and lower adjacent regenerative beds of relatively smaller bodies, and heating said intermediate bed to a high temperature sufficient to induce the oxidation of nitrogen by injection of a fluid combustible adjacent the junction of said intermediate bed with that regenerative bed which is first contacted by said gas, said fuel being injected only during the upward runs, and recovering nitric oxide thus produced.

3. A method of producing nitric oxide from a gas mixture essentially comprising nitrogen and oxygen, which comprises as the first half of each complete cycle the steps of passing said gas mixture serially through a preheating zone, an intermediate heating zone and a chilling zone, in the preheating zone passing the mixture through the interstices of a first bed of chaotically disposed relatively small refractory bodies heated by a previous cycle, during which step the gas mixture is heated and simultaneously the relatively small refractory bodies of said first bed are cooled, in the intermediate heating zone supplying heat for endothermic reaction by injecting fluid fuel into and burning the same in the gas mixture, and in said chilling zone passing the gas mixture through the interstices of a second bed of chaotically disposed relatively small refractory bodies cooled by a previous cycle, during which step the gases are rapidly cooled to a NO-stable temperature by transfer of heat to the refractory bodies in said second bed, and as the second half of each complete cycle reversing the direction of passage of the gas mixture serially through said zones while omitting injection of fuel into said gas mixture, the amount of fuel injected into said gas mixture during the aforesaid first half of

each complete cycle being such as by its combustion to maintain nitrogen-fixing temperature in said intermediate heating zone during the succeeding second half of the cycle.

4. The method defined in claim 3, in which the nitrogen-oxygen gas mixture passed serially through the preheating zone, intermediate heating zone and chilling zone during that half of the complete cycle during which fluid fuel is not injected into said gas mixture is substantially free from moisture.

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