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PATENT SPECIFICATION

Convention Date (United States): June 4, 1935. **471,931**

Application Date (in United Kingdom): March 13, 1936. No. 7686/36.

(Patent of Addition to No. 449,050: Dated June 1, 1934).

Complete Specification Accepted: Sept. 13, 1937.

1211

COMPLETE SPECIFICATION.

Operation of Catalytic Converters.

We, HOUDRY PROCESS CORPORATION, of 19, Dover Green, Dover, Delaware, United States of America, a corporation duly organized and existing under the laws of the State of Delaware, United States of America (assignees of EUGENE JULES HOUDRY and THOMAS BALDWIN PRICKETT), do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present addition has as its object the further utilization of the invention described in the principal patent No. 449,050 and additions thereto, viz., patent No. 456,091 and application for patent No. 7685/36 (Serial No. 471,930).

This invention relates to temperature control of reaction vessels. It is more particularly concerned with controlling the temperature of portions of a reaction chamber or zone containing a contact mass which may promote, enter into, or in any way assist chemical transformations. The invention is especially directed toward converters having operative cycles comprising alternate periods of exothermic and endothermic reactions or alternate periods on-stream and in regeneration.

One object of the invention is to hold a wall of the reaction chamber at substantially constant temperature during both periods of the operative cycle, thereby to prevent adjacent portions of the bed of contact mass or catalyst within the reaction chamber from being over-cooled or over-heated. Another object is to prevent large internal stresses in the wall and other portions of the converter and warpage or deformation caused by such stresses. Still another object is to maintain those portions of the contact mass adjacent the chamber wall at reaction temperature during the exothermic phase of the operative cycle, as well as during the endothermic phase thereof. Still further objects will be apparent from the detailed discussion which follows. In carrying these objects into effect it is necessary to remove large quantities of heat from the bed of catalyst or contact mass during the exothermic portion of the cycle of operation, and possibly to add substantial quantities of heat thereto during the endothermic portion thereof. An advantageous method of and apparatus for effecting this addition or removal of heat are described and illustrated in the specification of the said principal Patent showing heat exchange means imbedded in the contact mass and distributed throughout the same for effecting exchange of large quantities of heat while maintaining the temperature throughout the depth and cross-section of the bed substantially uniform. Since the practical use of the present invention necessitates the removal or addition of large quantities of heat, this invention has practical utility only in connection with such a process of heat transfer and has special advantage in connection with such a process of (and apparatus for) heat exchange as is taught in the specification of the aforesaid principal Patent, of which the present invention is an improvement or modification.

In one form of converter to which the invention is directed the fluid reactants for each period of the operation cycle are admitted to a manifolding chamber or zone in contiguity with the reaction chamber or zone and separated from the latter by a perforated partition extending across the converter. The reactants then pass through the partition and into the mass. If desired, they may be distributed throughout the depth and cross section of the mass by any suitable means, including perforated conduits such as disclosed and claimed in our prior Patent No. 414,779, dated May 14, 1932.

The temperatures of those portions of the converter shell bounding the manifolding chamber and of the face of the perforated partition toward that chamber closely follow the temperature of fluids contacting them. The temperature of the contact mass adjacent the partition or tube sheet also tends to follow the temperature of fluids admitted to the manifolding zones, though less closely than the tube sheet itself. The temperature of the

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main body of the contact mass is controlled to some extent by the temperature of entering reactants, but tends to go up or down with exothermic or endothermic reactions, respectively, the amount of temperature variation depending on the intensity of these reactions and the rate at which heat can be supplied to or removed from the mass. Those portions of the converter forming the reaction chamber vary in temperature with the contact mass. In instances where the reactions effected in the presence of the contact mass are strongly endothermic or exothermic in character, the temperature of the mass may be controlled by supplying heat thereto or removing heat therefrom as by circulating one or more streams of fluid in heat exchange relation with the mass as indicated for example in the specification of the said principal Patent No. 449,050, of which the present application is a modification or further development.

The walls of the manifolding chamber in a converter operating in an endothermic transformation at elevated temperature assume approximately the temperature of the entering reactants. When lower temperature fluid reactants for a subsequent exothermic reaction at the same or a higher temperature are admitted to the manifolding chamber the wall temperatures of the latter drop sharply toward the temperature of these fluids while the temperature of the mass adjacent the manifolding chamber drops slowly or, in some instances, may even rise. Thus, portions of the converter common to the manifolding and reaction chambers, as for example, the perforated partition and the converter walls, are subjected to internal stresses, caused by unequal rates of contraction within themselves or even opposed contraction and expansion. In some instances, these stresses become high enough to cause deformation of warpage of these portions of the converter. It is evident that when the transition is from exothermic to endothermic reactions unequal and non-compensating rates of expansion and contraction also tend to produce warpage of the converter structure. Stiffening or supporting members are sometimes provided for the perforated partition, particularly when the latter supports the weight of the contact mass and/or a series of fluid distributing members. In such instances, the tendencies of the partition to deform with changes in temperature of fluids entering the converter are intensified. The supporting members themselves are subject to deformation and/or pulling loose from their supporting fastenings with these temperature changes.

These problems or difficulties are in addition to the equally or more serious problems of keeping the bed of contact mass at substantially uniform temperature throughout every portion thereof, and especially adjacent the tube sheet or sheets, so that the bed of mass will be uniformly regenerated during the regeneration period and each portion thereof will possess uniform activity during the on-stream or reaction period. This latter problem is especially difficult to solve satisfactorily where reactants are supplied at a temperature substantially above the reaction temperature desired during the endothermic portion of the cycle of operation to supply heat absorbed in the process and where the other reactants or regenerating medium are supplied at a temperature much below that desired in the mass during the exothermic reaction.

The present invention avoids this difficulty and corrects the undesirable temperature conditions by control of the temperature of the reactions, i.e. by feeding fluid reactants for each period of the operation cycle to the converter at or near the same temperature, and removing heat from or supplying heat to the bed of mass by a separate heat exchange medium in the manner disclosed in our aforesaid patent, of which this is an addition or modification. The reactants for the endothermic reaction are heated to reaction temperature or slightly above and admitted to the manifolding chamber and thence to the contact mass and for the subsequent exothermic reaction the reactants are heated to the extent necessary to maintain the walls of the manifolding chamber at a substantially constant temperature, thus avoiding rapid and extensive changes in temperature of these portions of the converter structure with respect to other portions thereof. In addition to the above function, the heated reactants for the exothermic reaction period perform the further important function of maintaining the mass adjacent the perforated partition at a temperature level more nearly coincident with that of the main body of the mass.

One application of the invention is in the utilization of a contact mass alternately in transformation or treatment of hydrocarbons at one temperature level, say 750 to 900° F. and in regeneration at a higher temperature, as at 900 to 1100° F. According to this invention the hydrocarbons are usually heated to slightly above reaction temperature, as to 770° to 925° F., and fed to the converter during a transformation period. In the subsequent regeneration, the regenerating medium, as for example, a stream of oxygen bearing fluid, such as air or a mixture of air and inert gaseous diluents, is heated in any desirable manner to bring it within or near the temperature of the stream of hydrocarbons, as to 750° to 850° F. The inlet temperature of the regenerating medium is determined by the desired temperature for the walls of the manifolding chamber, especially the perforated partition. Following a hydrocarbon transformation effected at substantially 825° F., and during a regeneration at about 1050° F., an inlet temperature of the regenerating medium of approximately 800° F. holds the partition at substantially 825° F. Any lowering of the temperature of the partition has the deleterious effect of tending to check or retard the rate of regeneration of the mass which is adjacent the partition, thus tending to cause non-uniformity of regeneration throughout various portions of the bed of contact mass.

Concrete embodiments of the invention are disclosed in the accompanying drawings, in which Fig. 1 is an illustration of one form of the invention showing a preferred form of the converter in section. Fig. 2 is a diagrammatic representation of a modified form of the invention, and Fig. 3 is a diagram representing a still different modification.

In Fig. 1 converter X preferably covered with suitable heat insulating material such as lagging 4 is divided into end manifolding chambers A and B and centrally located reaction chambers C by perforated partitions or flue sheets 5 and 6. Fluid reactants for either exothermic or endothermic reactions supplied selectively by valved lines 17 or 22 pass through tee 18 to enter manifolding chamber A and are distributed uniformly throughout the depth and cross section of contact mass M disposed in reaction chamber C by a series of nested distributing members or perforated conduits 7 while fluid reaction products are simultaneously vented from a plurality of points in mass M into a series of perforated outlet conduits 8, substantially as described in the aforesaid British Patent No. 414,779. Mass M may be of any known or desired type capable of effecting the transformation or treatment of the starting material but is preferably in the form of bits, fragments, or molded pieces for regeneration in place and when utilized in the transformation of hydrocarbons may conform to those disclosed in our prior Patent No. 416,025, dated March 23, 1932, and in the specification of our copending Patent Application No. 20,124, filed July 20, 1936 (Serial No. 478,216). In the copending application, last mentioned, illustrative catalysts or contact masses are described which may be composed of silicious materials or blends of silica and alumina, whether of natural origin or artificially prepared (for example a blend of silica and alumina in which the weight ratio of silica to alumina is of the order of 4:1), which have present therein a small proportion (1% or 1.5%, more or less) of a metalliferous oxidation promoter, exemplary of which are metals or metal compounds of nickel, copper, cobalt, chromium, iron and manganese. The catalytic mass may be molded into pieces of regular size and shape having a penetration depth of the order of 1 mm.; for example, it may be molded into cylindrical pellets having a diameter of the order of 2 mm. The fluid reaction products are discharged into manifolding chamber B and thence into tee 11 to enter valved line 12 or valved line 13. Nested conduits 9 and 9*a* embedded in mass M serve to conduct a plurality of streams of cooling or heating fluids by reversed flow in heat exchange relation with mass M to remove heat from the latter during the exothermic reaction period and/or to supply heat to mass M during the endothermic reaction period. These nested conduits are of the type illustrated or described in considerable detail in our aforesaid Patent No. 449,050, or, of an equivalent type which permits circulating a fluid medium in heat exchange relation with but substantially out of heat conducting relation with the mass M. Manifolds 10 and 10*a* in nested relation supply the heat exchange fluid to and remove this fluid from conduits 9 and 9*a*. A continually fresh supply of heating or cooling fluid may be used, or the fluid may be recirculated through conduits 9 and 9*a* and a suitable cooling system, as for example, the circuits described in the specification of our aforesaid Patent No. 449,050.

Partition 5 is provided with ribs or stiffening members 14 to assist it in supporting the weight of contact mass M and conduits 7. Members 14 may be an integral part of partition 5, substantially as shown or they may be individual members attached, if desired, to partition 5 in any suitable manner and supported from the latter or the walls of converter 4 or both. Whether attached to partition 5 or not or supported from the latter and/or the walls of manifolding chamber A it is important that members 14 be maintained at substantially the temperature of partition 5 to prevent deformation of these members and/or loosening of their supporting fastenings.

Reactants for the endothermic transformation are conducted by line 15 from a suitable source of supply to heater 16 of any suitable type, wherein they are heated to the desired reaction temperature or slightly above, as to 750° to 925° F., in instances where the charge comprises certain types of hydrocarbon materials, as for example, light and heavy oils or vapors. The heated reactants are then conducted through valved line 17 and inlet tee 18 into manifolding chamber A, whence they are admitted to reaction chamber C, as described above. The reaction products are vented from the converter through outlet tee 11 and into valved line 12 leading to equipment for recirculation, storage, heating, cooling, fractionation, or any other desired treatment.

Reactants for the exothermic reaction are fed into a heater 21 by line 19 where they are heated to substantially the temperature of the endothermic reactants by direct or indirect heat exchange with combustion products from a suitable fuel conducted to heater 21 by line 20. The exothermic reaction products are vented from the converter through outlet tee 11 and line 13. Regenerating medium, such as air, is efficiently and economically raised to the desired temperature, to 800° F., for example, in direct heat exchange with combustion products from a fuel, as by commingling with and supporting combustion of a controlled amount of the latter. The direct heat exchange heater avoids the difficulties and expense of the erection, operation and maintenance of certain indirect heat exchange furnaces, such as pipe stills or the like, which often must be constructed of expensive alloy steels, particularly when they are intended to handle air and corrosive fluids at high temperatures.

Whereas, in the embodiment disclosed in Fig. 1, the exothermic reactants are heated to the desired temperature in a single stage, Fig. 2 illustrates two stage heating of these reactants. Exothermic reaction products leaving converter X*a* by valved line 13*a* enter heat exchanger 23*a* wherein they impart heat to the exothermic reactants being supplied by line 19*a*. The heated reactants are further heated to the predetermined temperature level in heater 21*a* of any desirable type and are conducted thence into converter X*a* by valved line 22*a*. The temperature of the regenerating fluid may be raised to the range of 300 to 600° F. in exchanger 23*a* and to the range of 750 to 850° F. in the second stage heater 21*a*.

In Fig. 3, the exothermic reactant fluids, such as air or the like are supplied by line 19*b*. The fluid is split into two streams which flow through valved conduits $19b^1$, and $19b^2$, respectively, the proportionate amounts of these two streams being controlled by the valves in conduits $19b^1$ and $19b^2$. One stream is conducted into combustion chamber $21b^1$ of heater 21*b* where it commingles with fuel supplied by line 20*b* and is heated to a predetermined temperature in direct heat exchange relation with the burning fuel. The stream of combustion products passes through line 24*b* to be commingled with the air stream in line $19b^2$. The combined streams then pass through conduit 25*b* into pipe coil 26*b* where they are in indirect heat exchange relationship with the combustion mixture in chamber $21b^1$ to complete heating of the regenerating medium to the desired temperature before admittance to the converter through conduit 22*b*.

With control of the proportionate amounts of regenerating medium heated by indirect heat exchange alone and by both direct and indirect heat exchange, this fluid can be simultaneously heated to the desired temperature, such as 750° to 850° F. and commingled with a predetermined and controlled amount of diluting combustion fumes.

It is apparent from the above that the invention presents improvements in the use of processes in which a bed of contact or catalytic mass is employed and in the operation of converters which simplify problems met in the design and use of the same. The invention is not limited in its essence to the specific forms and examples disclosed herein for the purpose of illustration and explanation. The converter may be of any type adapted for processing fluids, as described in the said principal Patent and especially may be of the type which has a manifold or manifolding chamber adjacent a reaction chamber containing or adapted to contain a catalytic mass where the reaction chamber is separated from the manifolding chamber by a perforated partition or tube sheet. The invention is applicable whether the converter is operated in horizontal, oblique, upright or inverted position.

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that what we claim is:—

1. Process of operating a converter having a reaction zone containing a contact mass capable of use in a cycle of alternate periods of endothermic and exothermic reactions, the converter hav-

ing a manifolding zone adjacent the reaction zone and heat exchange means within the reaction zone for controlling the temperature of the contact mass, in accordance with the principal patent No. 449,050 and additions thereto, viz., Patent No. 456,091, and application for Patent No. 7085/36 (Serial No. 471,930), characterized by alternately admitting fluid reactants to the manifolding zone for each period of the cycle at such temperatures as to maintain portions of the converter common to the zones at substantially constant temperature.

2. Process according to claim 1 further characterized by feeding heated hydrocarbons for an endothermic transforming reaction and subsequently feeding a regenerating medium for an exothermic regenerating reaction, the regenerating medium being heated substantially to the temperature of the hydrocarbon charge.

3. Process according to claim 2 further characterized by feeding the hydrocarbon charge at a temperature of 770° to 925° F. and subsequently feeding the regenerating medium at a temperature of 750° to 850° F.

4. Process according to any of the preceding claims further characterized by heating the regenerating medium to approximately 800° F. before sending it into the manifolding zone.

5. Process according to claim 4 further characterized by bringing the regenerating medium to the desired temperature in two stages, the first stage raising the medium to a temperature between 300° and 600° F. and the second stage raising it to 750° F. or above.

6. Process according to claim 5 further characterized by utilizing the fumes of regeneration to supply some or all of the heat for the first stage through indirect heat exchange and/or commingling of hot fumes with the regenerating medium.

7. Process according to claims 2, 3 and 4 further characterized by commingling at least a part of the regenerating medium with a controlled and predetermined amount of fuel and burning the fuel and sending the regenerating medium and the combustion products of the fuel into the contact mass to regenerate the same.

8. Process according to any of claims 2, 3 and 4 further characterized by dividing the stream of regenerating medium into two portions, heating the first portion and diluting it by adding hot products of fuel combustion, commingling the heated and diluted first portion with the second portion, and then heating the commingled portions by heat exchange with the combustion products.

9. Converter with connections and controls substantially as shown in Fig. 1.

10. Converter with connections and controls for endothermic and for exothermic reactants substantially as shown in Fig. 2.

11. Converter with connections and controls for exothermic reactants or a regenerating medium substantially as shown in Fig. 3.

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Chartered Patent Agents.

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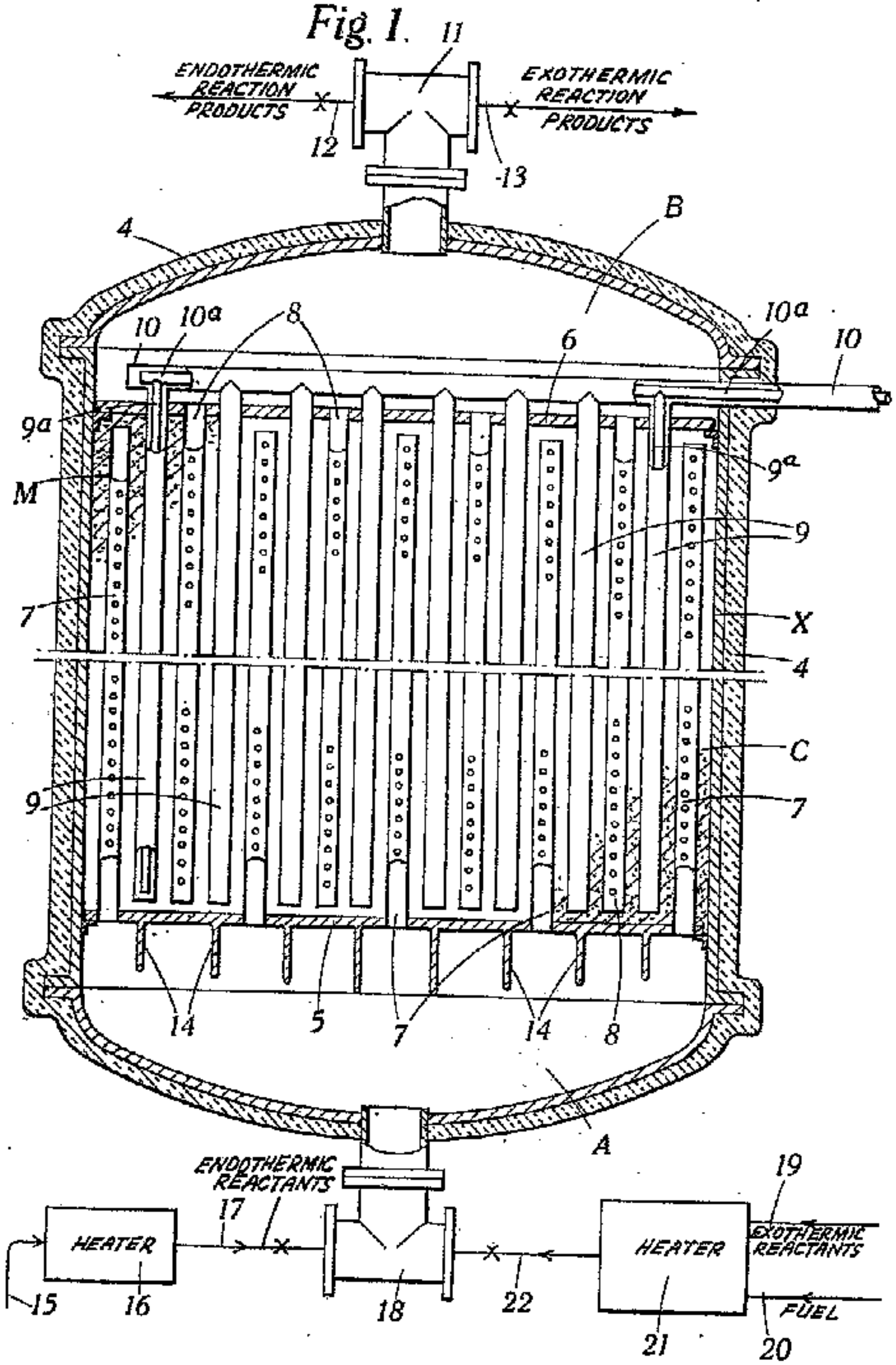
[Wt. 8030.—50/6/1938.]

Fig. 1.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HEATER
HEATER
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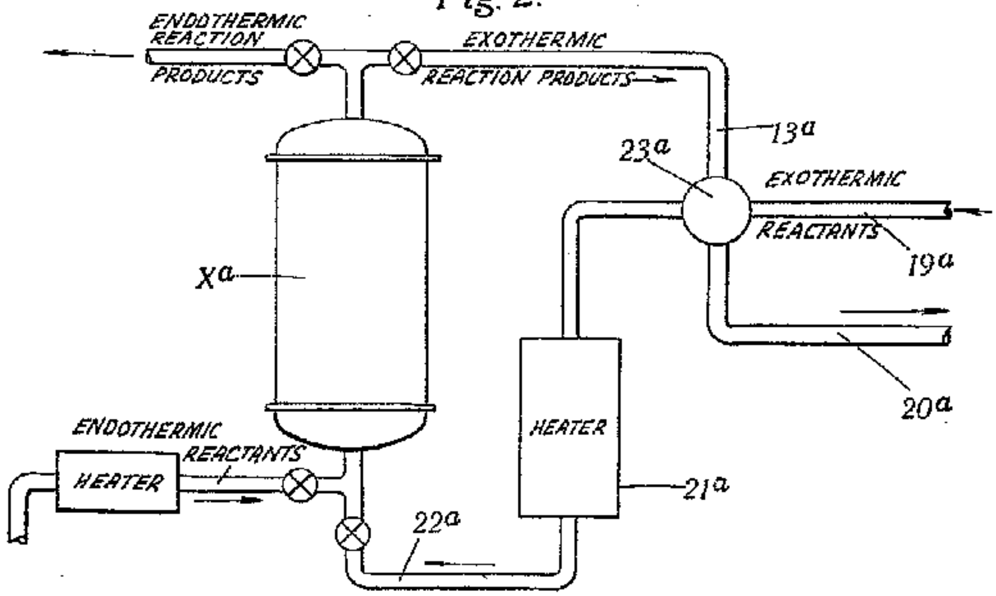
EXOTHERMIC REACTANTS
FUEL

Fig. 2.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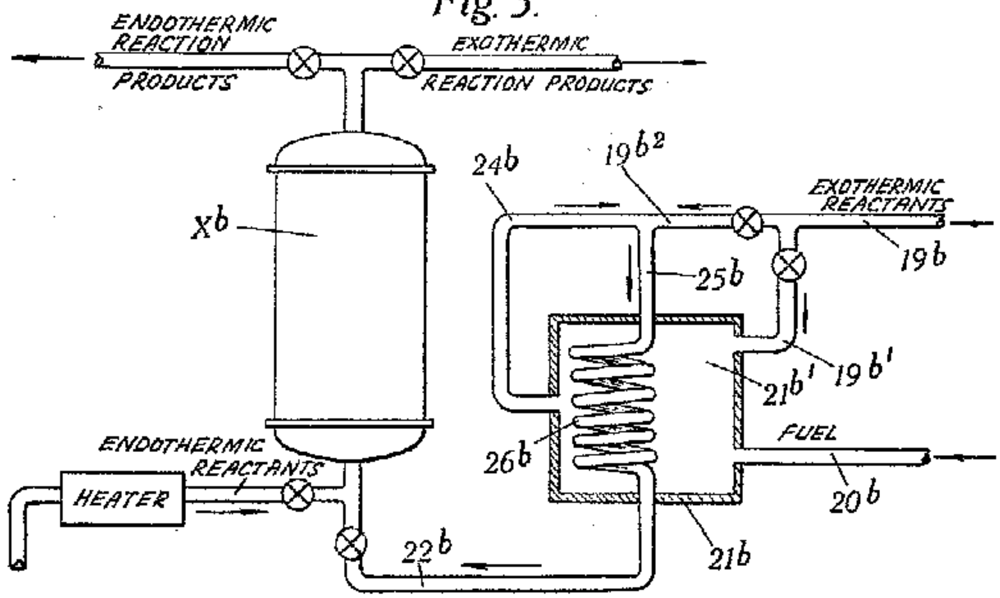
22a

Fig. 3.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19b1
FUEL
26b
20b
ENDOTHERMIC
REACTANTS
HEATER
22b
21b

471,931 COMPLETE SPECIFICATION

2nd Edition

SHEET 1

2 SHEETS
SHEET 2

Fig. 1.

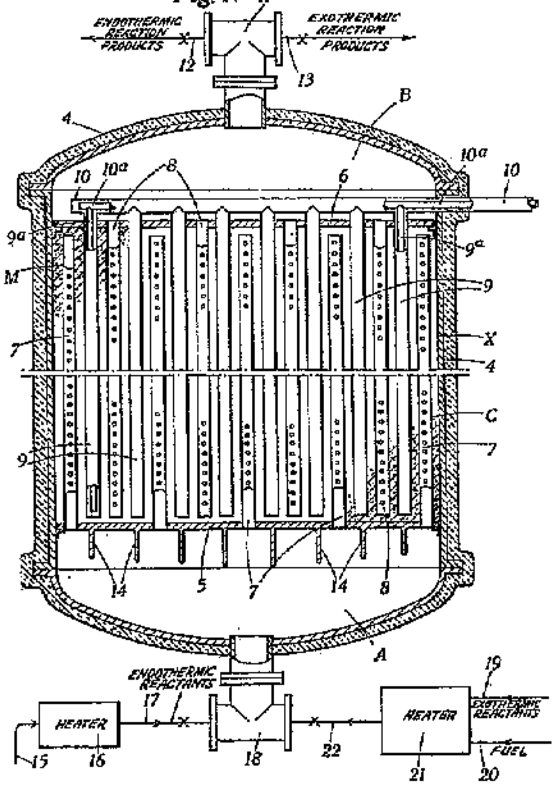


Fig. 2.

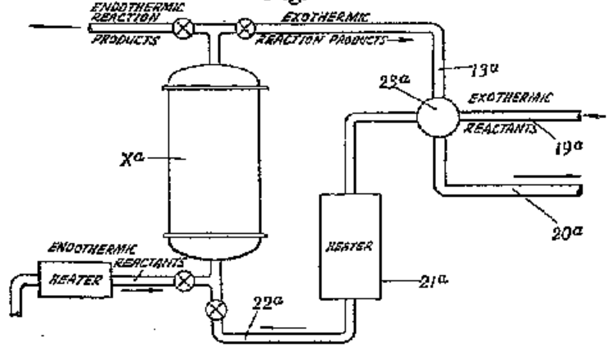
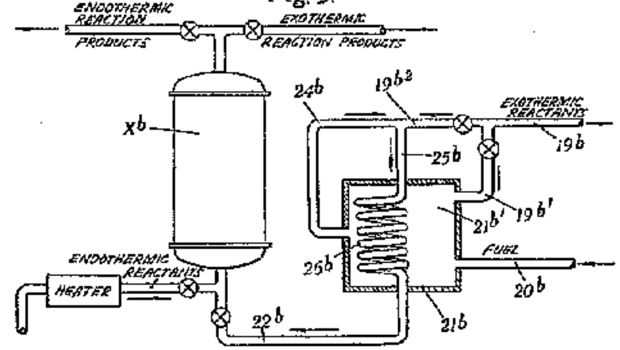


Fig. 3.



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