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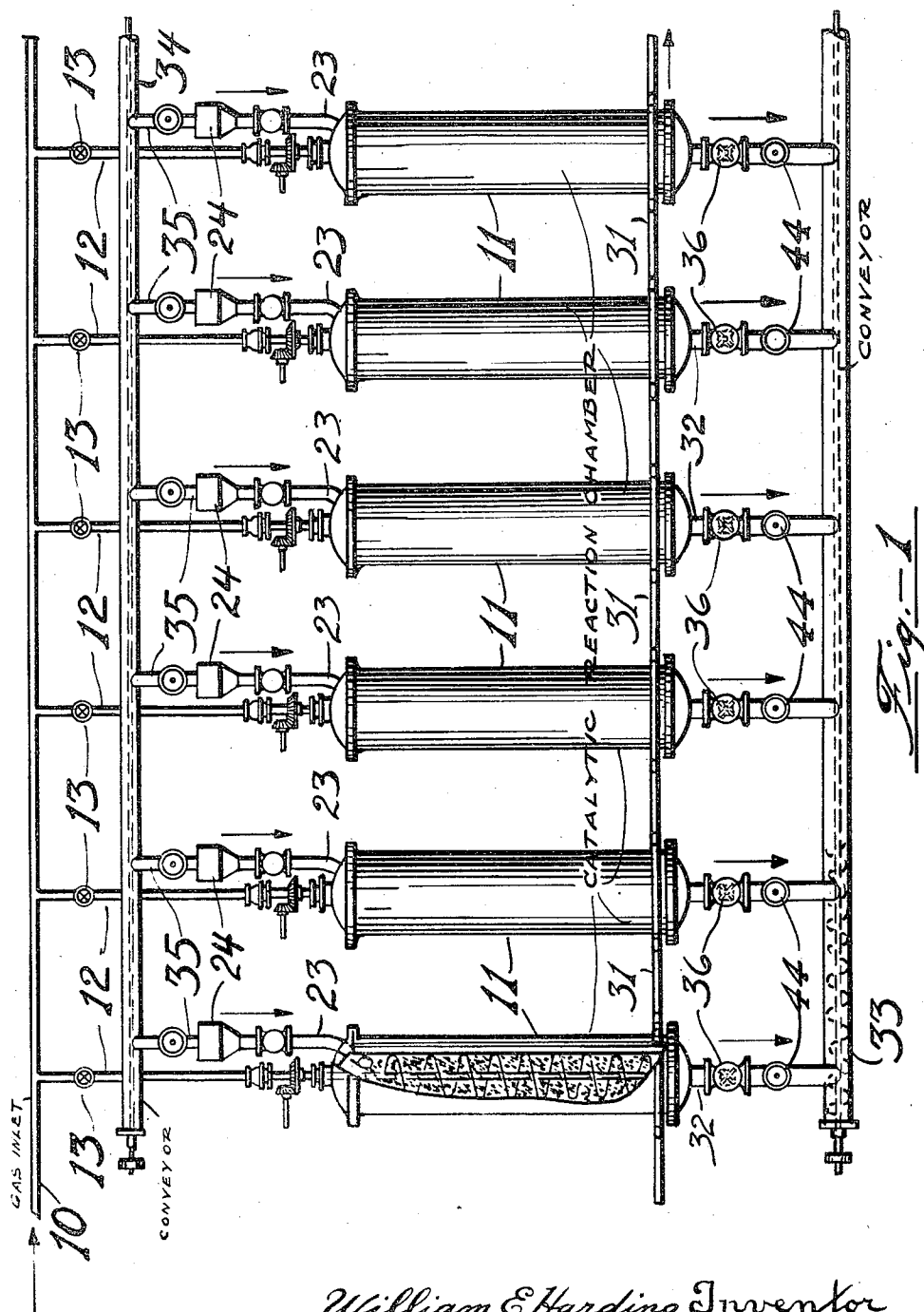
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2,265,837

METHOD OF AND APPARATUS FOR CARRYING OUT CATALYTIC PROCESSES

Filed Nov. 13, 1937

3 Sheets-Sheet 1



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3 Sheets-Sheet 2

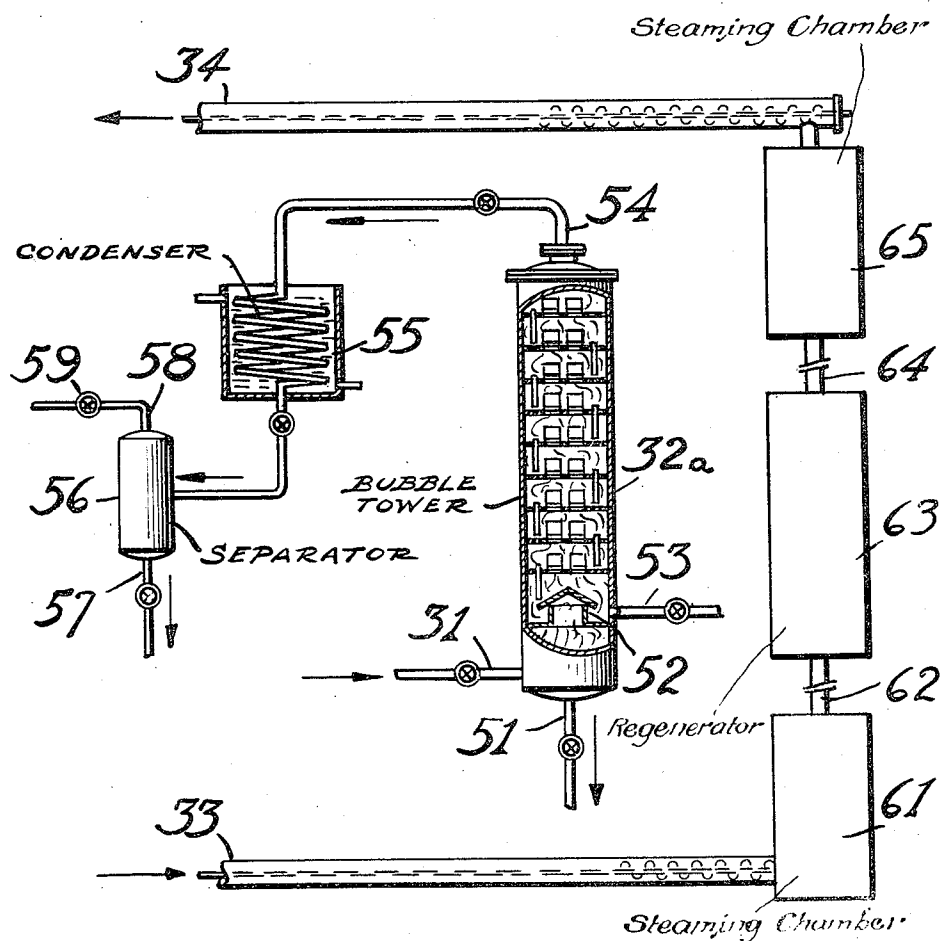


Fig. - 2

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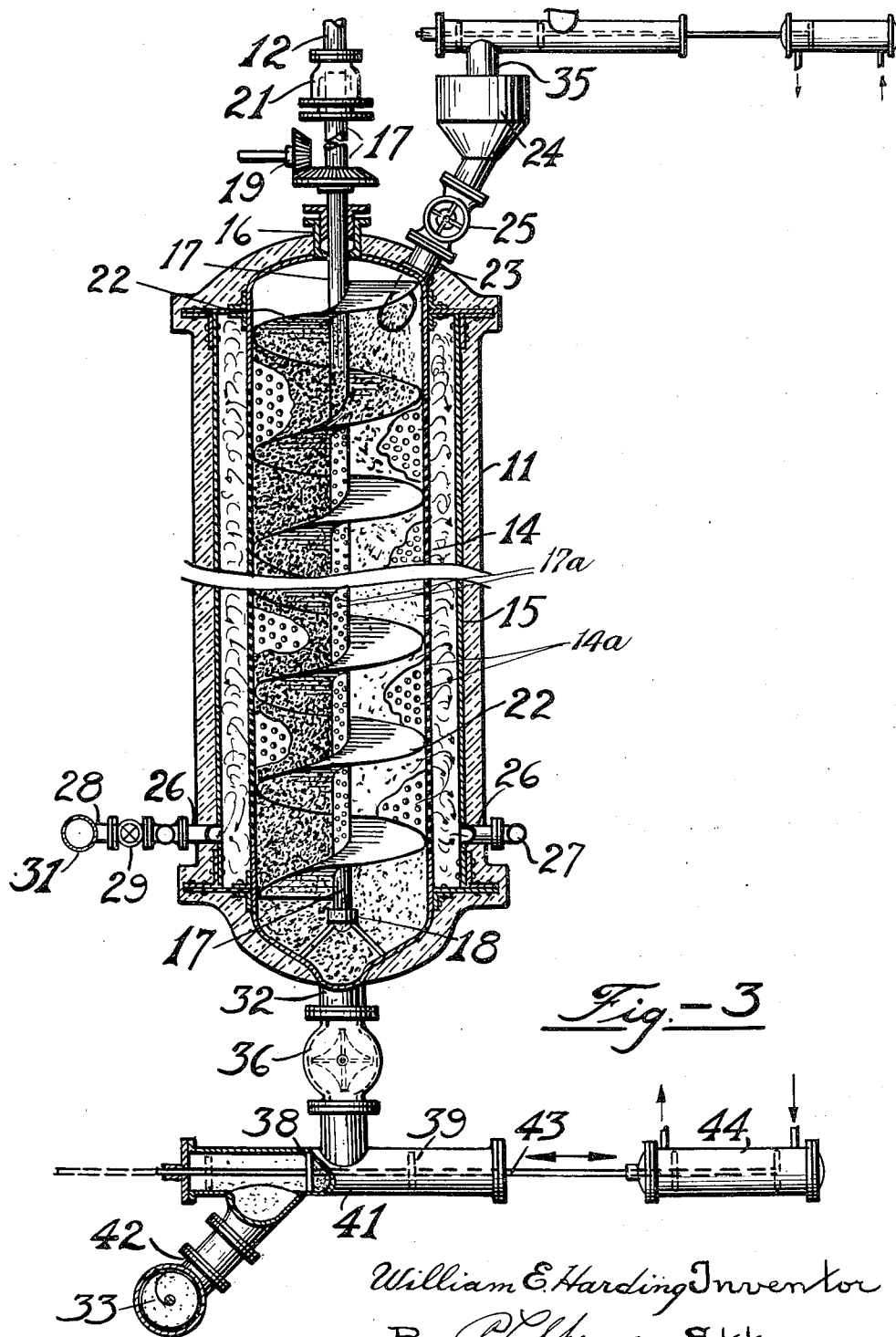
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3 Sheets-Sheet 3



UNITED STATES PATENT OFFICE

2,265,837

METHOD OF AND APPARATUS FOR CARRY-
ING OUT CATALYTIC PROCESSESWilliam E. Harding, Plainfield, N. J., assignor to
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Application November 13, 1937, Serial No. 174,429

4 Claims. (Cl. 196—52)

This invention relates to a method of and apparatus for carrying out catalytic reactions which require regeneration of the catalyst to restore its activity and pertains more particularly to a method and apparatus which will permit the process to be carried out continuously as distinguished from intermittent processes in which the reaction and regeneration is accomplished in cycles of these two alternating operations.

While this invention in some of its broader aspects will have a more general application, it is of particular advantage for catalytic treatment of hydrocarbons, such as catalytic cracking and polymerization.

It has heretofore been discovered that cracking oil in the presence of certain types of adsorptive catalysts such as naturally active clays or clays made active by acid or other suitable treatment and certain types of synthetic gels results in the production of gasoline having high anti-knock properties. However, during the cracking operation, the activity of the catalyst is rapidly reduced due to the formation of solid carbonaceous deposits on the surface of the catalyst.

In order to restore the activity of the catalyst, it becomes necessary to periodically remove the carbonaceous deposits so formed. The removal can be effectively accomplished by burning the catalyst with an oxidizing gas such as air or a mixture of air and steam.

According to one mode of operation heretofore proposed the regeneration is carried out within the same chamber in which the cracking is accomplished in alternate cracking and regenerating steps. In order to operate such a process continuously, it is necessary to provide a plurality of reaction chambers with manifold lines so that any one or more of the reaction chambers may be operating on the cracking stream while the remainder are undergoing regeneration.

In addition to the actual time required for regeneration, there is a further substantial time loss between the cracking and regenerating steps and vice versa, necessary to condition the catalyst bed. For example, after the cracking has been discontinued and before the regeneration is begun, it is necessary to remove volatile oil constituents absorbed by the catalyst to prevent possible explosions resulting from contacting the hot volatile oil with the regenerating gas. This may be accomplished by steaming the catalyst to vaporize the oil. Following the regeneration, it is also desirable to steam the catalyst to remove oxygen or other products of regeneration before returning the catalyst chamber to the

cracking stream. Moreover, the cracking and regenerating steps may operate at different temperature levels which requires additional time to bring the catalyst to the required temperatures between the steps.

For these and other reasons, such an intermittent cracking process requires additional reaction chambers over that required if cracking could be carried out continuously without interruption for regeneration.

In addition to the intermittent cracking and regeneration process heretofore mentioned, it has also been suggested to continuously remove spent catalyst from the reaction chamber and regenerate the same outside the reaction chamber and continuously introduce spent and fresh catalyst without interrupting the cracking. For example, it has been suggested to suspend the catalyst in finely divided form in the vapors to be cracked during their passage through the reaction chamber and subsequently separating the vapors from the catalyst. In order to effectively separate the catalyst from the vapors, expensive separating equipment is required and it is difficult to properly control the time of contact between the vapors and the catalyst.

One of the important objects of the present invention is to provide a process for carrying out catalytic cracking and polymerization and other analogous chemical reactions in a continuous manner.

Another important object of this invention is to provide a continuous process for catalytically cracking oil which will require a smaller amount of equipment for a given capacity and which will reduce installation and operating costs.

Another important object of this invention is to provide a continuous process for the catalytic cracking of oil which will permit a more accurate control of contact time between the oil vapors to be cracked and the catalyst bed.

A further object of the invention is to provide an improved apparatus for catalytic cracking and other similar catalytic reactions in which it is necessary to regenerate the catalyst frequently.

A further object of the invention is to provide an apparatus for catalytic conversion which will permit more effective control of the cracking conditions.

Other more specific objects of my invention will become apparent from the more detailed objects.

In accordance with the broader phases of my invention, the catalyst bed is caused to pass progressively through the reaction zone in a solid

relatively compact form, at any desired rate of speed. According to the more specific aspects of the invention, the catalyst mass in relatively compact form is conveyed through the reaction zone at any desired rate of speed and the vapors to be reacted pass through a uniform depth of catalyst mass and in a direction transverse to the general direction of movement of the catalyst mass. According to further phases of my invention the catalyst mass is conveyed through the catalytic zone, then subjected to conditioning and regenerating equipment in which the activity of the catalyst is restored and is then returned to the catalytic chamber in a continuous manner.

Various other objects and advantages of the invention will be apparent from the more detailed description hereinafter, in which reference will be made to the accompanying drawings.

In the drawings, Figure 1 is a side view of a battery of catalytic reaction chambers constructed in accordance with the invention showing parts in section and conveyors for introducing and removing catalysts to and from the chambers.

Figure 2 is a continuation of Figure 1, showing diagrammatically a system for treating and regenerating the catalyst and for the recovery of reaction products, and Figure 3 is a sectional view of the catalytic reaction chambers shown in Figure 1.

Referring to Figure 1, the numeral 10 indicates a charging line for introducing the gases to be reacted into a bank of catalytic chambers 11. To this end, the charging line 10 is provided with separate branch lines 12 provided with valves 13 leading to each of the catalytic chambers 11. The reaction chambers 11 shown in Figure 1, are all of the same construction, so that a description of one of the chambers will suffice for all.

Referring to Figure 3, the catalyst chambers 11 comprise an inner metallic shell 14 having perforations 14a and an outer spaced concentric shell 15. The space between the inner and outer shells 14 and 15 forms a vapor space for the collection of vapors removed from the catalyst zone. The outer shell 15 is lagged with suitable insulating material to reduce radiation losses. Extending downwardly through a stuffing box 16 in the top of the inner shell 14 is a central hollow shaft 17 having perforations 17a terminating in a thrust bearing 18 supported at the bottom of the inner shell 14. The hollow shaft 17 is provided with suitable means for effecting rotation thereof, such as a pinion gear 19 located at the top thereof. Branch lines 12 leading from the charging line 10 are connected with the rotary shaft 17 at the upper end thereof through a suitable stuffing box 21 to provide a sealed communication between the branch lines 12 and the hollow shaft 17 so that the gases to be reacted are introduced into the reaction chamber through the central rotary shaft 17.

The hollow shaft 17 is provided with a spiral flange 22 forming a screw conveyor for forcing the catalyst through the reaction chamber. The catalyst is introduced into the top of the reaction chamber through a pipe 23 leading from a hopper 24. The pipe 23 is preferably provided with suitable valves 25 for controlling the rate of charging of the catalyst into the reaction zone. The catalyst, after being introduced into the reaction zone, is picked up by the flange 22, secured to the rotary shaft 17 and forced down-

wardly through the reaction zone. As shown in Figure 3, the upper convolution of the spiral flange 22 is of greater pitch than the other convolutions so that the catalyst is slightly compressed and more uniformly distributed throughout the full cross-sectional area of the catalyst zone before being introduced into the main treating section of the reaction zone.

The vapors introduced into the reaction chamber through the rotary shaft 17 pass through perforations therein into the bed of catalyst moving through the reaction zone and the reacting gases are caused to pass transversely through the catalyst bed and are exhausted through apertures in the inner shell 14. The reaction products after passing through the apertures are collected in the annular chamber formed by the inner shell and outer shells 14 and 15. The reacted gases are withdrawn from the annular chamber through a plurality of outlet ports communicating with pipes 26 at the bottom of the chamber. The pipes 26 connect at the outer ends with a bustle pipe 27 extending circumferentially of the reaction chamber 11. The bustle pipe 27 in turn connects through a line 28 provided with a valve 29 to a manifold line 31 through which the reaction gases are caused to pass to a suitable recovery system, such as a fractionating tower 32 (as shown in Figure 2) for separation of the desired products from the reaction gases.

As shown in Figure 3, the perforations in the inner shell 14 and in the rotary shaft 17 begin below the second convolution of the spiral flange 22 so that the upper section between the first and second convolutions of the spiral flange 22 does not form a part of the reacting section of the chamber 11. The space between the first and second convolutions forms a charging zone for the catalyst. By providing a greater pitch to the first convolution of the flange 22 the catalyst upon passing to the second convolution of the flange is forced into a smaller space and thus tends to fill any voids which may result from unequal charging of the catalyst, so that the catalyst may be uniformly distributed throughout the full cross sectional area of the reaction zone before coming in contact with the gases to be reacted.

The apertures in the rotary shaft 17 and in the inner shell 14 may be of uniform size and spaced throughout the full length of the reacting section of the chamber 11 as above described, or the size and spacing of the apertures may be graded to control the amount of the reaction products passing through different vertical sections of the reaction chamber. For example, as the catalyst progresses through the reaction zone its activity gradually becomes reduced due to formation of carbonaceous deposits. These carbonaceous deposits, however, increase the density of the catalyst mass and hence the resistance of the catalyst to the flow of gases therethrough. As a consequence, when the apertures are of uniform size and spacing, a relatively larger proportion of gases will pass through the fresher catalyst per unit time. In this respect, my invention provides a more or less self compensating method of carrying out the treatment in that the time of control will vary inversely with the activity of the catalyst and thus tend to cause uniform conversion of the oil throughout the full length of the catalyst zone. However, the size of the apertures and the spacing therebetween may be so adjusted so as to cause more

or less of the vapors to pass through the top and bottom of the reaction zone as desired. Moreover, the pitch of the spiral flange passing through the catalyst zone may be gradually increased from top to bottom to compensate for increase in volume of catalyst due to formation of carbonaceous deposits so that the pressure drop through the catalyst bed is substantially uniform throughout the full length thereof. From the above, it will be noted that the volume of vapors passing through the different vertical sections of the catalyst zone may be controlled as desired by modifying the size and spacing of the apertures and the pitch of the spiral flange 22.

As shown in Figure 3, the apertures both in the rotary shaft 17 and in the inner shell 14, may be inclined to reduce plugging of the apertures with catalyst material.

The catalyst, after passing through the reaction zone, is withdrawn from the bottom of the chamber through line 32 leading to a common screw conveyor 33 adapted to receive catalysts from each of the reaction zones. The screw conveyor 33 is adapted to convey the catalyst to a suitable recovery apparatus, illustrated diagrammatically in Figure 2, for the treatment and regeneration of the catalyst.

The catalyst, after being reactivated, is returned to the reaction chambers through a suitable conveyor, such as a screw conveyor 34 which discharges the catalyst through branch pipes 35 into the hoppers 24. Positioned in the outlet line 32 for withdrawal of catalyst from the reaction chambers and the branch lines 35 for introducing the fresh catalyst into the hoppers 24, are suitable means for maintaining a differential pressure between the catalyst chamber and the conveyors 33 and 34. Any suitable pressure seal may be provided in these lines. As shown at the bottom of Figure 3, the pressure seal may comprise a rotary valve 36 coupled with a reciprocating valve, having two spaced plungers 38 and 39 adapted to reciprocate within a cylinder 41 and form a seal between the conveyor line 33 and the reaction chamber. The cylinder 41 communicates by means of line 42 leading to the conveyor 33 from which the catalyst is passed to a suitable regenerating system. The plungers 38 and 39 are secured to a piston rod 43 operated by suitable reciprocating mechanism, such as a hydraulic piston 44. The plungers 38 and 39 are so spaced on the piston rod 43 that when the piston rod is in the extreme forward position, the plunger 38 extends beyond the outlet pipe 42 and the plunger 39 is positioned between the inlet and outlet ports of the cylindrical section 41. When the piston rod 43 is in a retracted position, the advanced plunger 38 is positioned between the inlet and outlet ports of the cylindrical section 41 so that in either position of the plungers there is a seal between the conveyor 33 and the outlet line 32. The rotary valve 36 is operated to close communication between the outlet line 32 and the cylindrical section 41 during operation of the plungers 38 and 39.

Pressure seals of similar construction are provided in branch lines 35 leading from the charging conveyor 34 to the hopper 24 for each reaction chamber.

By providing pressure seals in the inlet and outlet of each reaction chamber, as above described, any desired pressure may be maintained within the reaction chambers or any one or more

of the chambers may be withdrawn from operation without interrupting operation of the remaining chambers. For example, by closing any one or more of inlet valves 13 in branch lines 12 and outlet valves 29 leading from the bustle pipe 26 to the manifold 31 and the rotary valves in branch lines 23, any desired number of reaction chambers may be withdrawn from operation. Rotary valves 36 in the outlet of the chambers withdrawn from operation may be continued to operate until the catalyst has been completely removed from the chamber after which the chambers may be inspected or repaired.

The invention will now be described with reference to the cracking of hydrocarbon oils, it being understood that in its broader aspects it will have a more general application.

The oil to be cracked is first vaporized in a suitable heating unit, not shown, and heated to the desired reaction temperature, after which it is introduced into the system through line 10 of Figure 1. The heated vapors introduced through line 10 are passed through any one or more of the branch lines 12 to the central hollow rotary shaft in the reaction chamber 11. The heated vapors thence pass through the apertures in the hollow shaft into contact with the catalyst, and pass through the catalyst bed in a direction transverse to the direction of the general movement of the catalyst through the reaction zone. The rate of flow of the oil vapors and the capacity of the reaction zone are controlled to provide the desired reaction time within the zone. The reaction products, after passing through the catalyst material, pass from the catalyst bed through apertures in the inner shell 14 into the annular vapor space surrounding the inner shell. By introducing the gases into the upper end of the rotary shaft and withdrawing the vapors from the bottom of the annular chamber all of the gases have substantially the same length of travel within the reaction chamber 11 from the point of entry to the point of withdrawal.

The reaction products are withdrawn from the annular chamber through pipes 26 and are collected in the bustle pipe 26 from whence they pass through lines 28 to a manifold line 31 leading to a fractionating tower 32^a. The gases, during their passage through the fractionating tower 32^a, are subjected to fractional condensation to condense constituents insufficiently cracked to motor fuel as condensate. The total condensate formed in the fractionating tower 32^a may be withdrawn from the bottom thereof from through line 51 or the fractionating tower may be provided with any desired number of trap out trays 52 for separately collecting individual fractions formed in the fractionating tower. For example, when recycling insufficiently cracked condensate to the cracking unit, it is sometimes desirable to recycle only a lighter fraction of the condensate and to separately withdraw from the system the highest boiling condensate formed. In such cases, the trap out trays 52 may be positioned to collect the desired condensate for recycling to the cracking unit and the collected condensate may be withdrawn through line 53 and recycled to the cracking zone through a line (not shown).

Vapors remaining uncondensed in the fractionating tower 32^a pass overhead through line 54 to a condenser 55 in which the desired distillate product is condensed. Products from the condenser 55 pass to a receiver 56 in which the

liquid distillate separates from the normally gaseous constituents. The distillate is withdrawn from the receiver 56 through line 57 and the gaseous constituents are vented from the system through line 58 provided with valve 59 for maintaining the desired back pressure on the cracking equipment. The distillate withdrawn through line 57 may be subjected to any desired further treatment for conversion into the final stabilized gasoline product.

The catalyst employed during the cracking operation may be any of the cracking catalysts, such as solid adsorptive contact material, for example, active or activated clays, such as fuller's earth or acid-treated bentonitic clays or synthetic gels. The catalyst may be in molded or finely divided form or deposited on a suitable inert carrier.

The activity of the catalyst within the reaction chamber is rapidly reduced due to the formation of carbonaceous deposits resulting from the cracking treatment. The movement of the catalyst through the reaction chamber is controlled by regulation of the speed of rotation of the shaft 17, so that the activity of the catalyst emerging from the bottom of the reaction zone is such that further treatment therewith is no longer desirable. The spent catalyst is then removed from the zone through the line 32 and conveyed by means of a screw conveyor 33 to a steaming chamber 61 in which the spent catalyst is subjected to distillation to remove volatile oily constituents from the surface of the catalyst. After being subjected to the desired steaming treatment, the catalyst is removed from the chamber 61 and introduced into a suitable regenerating chamber 63 in which the carbonaceous deposits on the catalyst are removed. The regeneration of the catalyst may be accomplished effectively by passage of an oxidizing medium, such as air or air diluted with steam, to burn off the carbonaceous deposits. The regenerating equipment may take a number of different forms and constitutes no part of the present invention. It is shown in the drawings only schematically. When regenerating catalysts, such as activated clays, it is desirable to accurately control the temperature of regeneration in order not to permanently reduce the activity of the catalyst. Any regenerating mechanism capable of effecting close temperature control over the catalyst during regeneration can be used. For example, the catalyst may be introduced into a conventional Herreshoff type of furnace in which the catalyst is caused to pass downwardly over a plurality of vertically spaced hearths in counter-current contact with hot oxidizing gases. The catalyst may be conveyed from one hearth to the other by the conventional rabble arms mounted on a rotary shaft within the furnace.

In addition to the Herreshoff type of furnace for effecting regeneration, the conventional type of sintering apparatus adapted for sintering low grades ores may be employed satisfactorily. This type of apparatus comprises generally a travelling grate conveyor passing through a combustion zone in which the air or oxidizing gas is passed through the grate for burning the material thereon. This type of apparatus is well adapted for controlling regeneration of the catalysts since the catalyst layer on the grate conveyor may be at any desired depth to effect close control of the combustion temperature. These sintering devices are commonly known in

the art as the Dwight-Lloyd sintering machines.

As a further example, a spent catalyst may be passed through a conventional rotary kiln through which the oxidizing gases are caused to pass. The regenerating mechanism is preferably a continuous one, wherein the catalyst may be continuously introduced and removed from the regenerating zone.

The regenerating catalyst, after withdrawal from the regenerating zone, is again introduced into a steaming zone which is indicated on the drawings as chamber 65, wherein the catalyst is subjected to distillation to remove regenerating gases from the surface thereof. This second steaming operation may be dispensed with if desired. The catalyst may then be passed from the chamber 64 to the screw conveyor 34 employed for conveying the catalyst to the hoppers 24 of the individual reaction chambers 11. The hoppers 24 are of sufficient capacity so as to provide a sufficient reserve supply of catalyst to permit the catalyst to be introduced into the individual reaction chambers at a uniform rate.

In the drawings, there is shown common conveyors for introducing and removing the catalyst to a bank of reaction chambers. It will be understood that the speed of the common charging conveyor 34 and the common discharging conveyor 33 may be synchronized so that the catalyst is charged and discharged from each chamber at the same rate. Moreover, the driving gear for the rotary shafts 17 in the reaction chambers may be operated independently or synchronized so that all operate at the same speed. Also, the driving gears for the rotary shaft 17 are preferably synchronized with the catalyst charging and discharging valves 25 and 35 so that the rate of charging and discharging is varied automatically with variations in speed of rotation of the shafts 17.

While I have shown common conveyors 33 and 34 for discharging and charging a bank of reaction chambers, it will be understood that separate conveyors may be employed for each reaction chamber or that a single reaction chamber may be used instead of a bank in accordance with certain phases of the invention.

Having described the preferred embodiment of the invention, it is understood that it embraces such other variations and modifications as come within the spirit and scope thereof.

In the accompanying claims, it is my intention to cover the invention as broadly as the art will permit.

I claim:

1. In the catalytic cracking of petroleum oil to produce motor fuel of high anti-knock properties wherein the oil to be cracked is passed in vapor form through a reaction zone containing a bed of cracking catalyst; the improvement which comprises progressively passing the bed of catalyst through the reaction zone and passing the oil vapors through said bed of catalyst in a direction transverse to the general direction of movement of catalyst through the reaction zone.

2. An apparatus for carrying out vapor phase catalytic reactions which comprises a metal shell forming a reaction chamber adapted to contain a bed of catalyst material having perforations in the side walls thereof, an outer jacket in spaced relation to the side walls of said reaction chamber forming an annular enclosed space surrounding said reaction chamber, a perforated conduit extending longitudinally within said reaction

chamber in spaced relation to the walls thereof, means integral with said conduit for moving the catalyst through the reaction zone, means communicating with said perforated conduit for introducing gases to be reacted and means communicating with said annular space for withdrawing reaction products.

3. An apparatus adapted to carry out vapor phase catalytic reactions comprising a reaction chamber adapted to contain a bed of catalyst having perforated side walls, a jacket surrounding said side walls in spaced relation therewith to form an annular chamber in vapor communication with said reaction chamber, a perforated conduit extending longitudinally within said reaction chamber, means for rotating said conduit, a spiral flange secured to said conduit adapted to move said bed of catalyst through the reaction chamber during rotation of said conduit, means for continuously charging said reaction chamber with catalyst, means for continuously removing catalyst from said chamber, means communicating with said perforated conduit for introducing

vapors to be reacted and means communicating with said annular space for removal of reaction products.

5 4. In an apparatus for contacting vapor with solid catalyst material, a chamber comprising a perforated tubular shell, a tubular jacket in spaced relationship thereto forming an annular space surrounding said chamber, a driven member comprising a hollow perforated shaft disposed substantially concentrically with respect to said chamber, a spiral flange integral with said driven member comprising a catalyst conveying means and extending substantially the entire length of the shaft within said chamber, means 10 for supplying a solid catalytic material to the reaction chamber at or near the top of said conveying means, means for introducing vapors into said hollow perforated shaft for conductance through the conveying means and separate means 15 for recovering the catalytic mass and the vapors respectively which have passed from the reaction chamber. 20

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