

April 2, 1946.

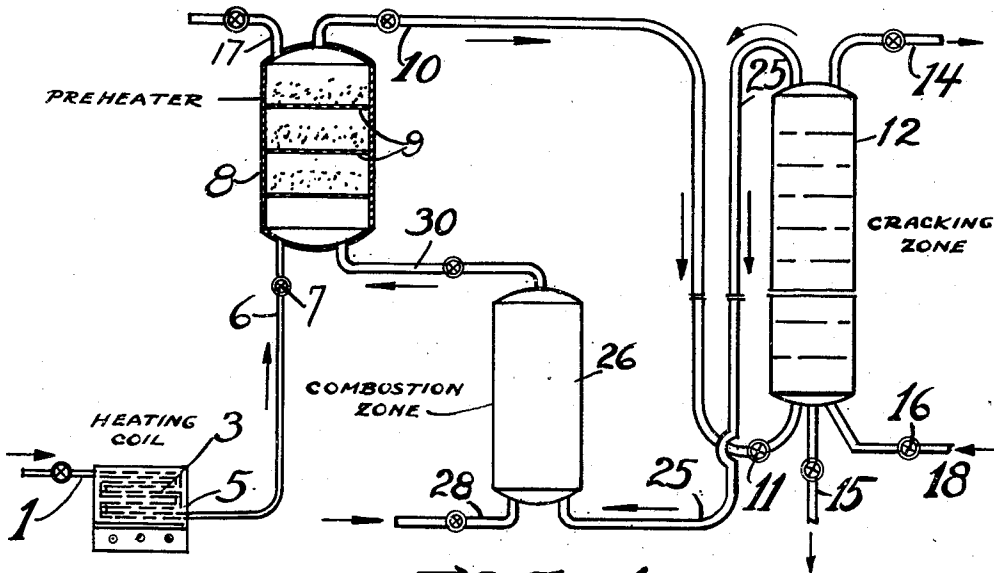
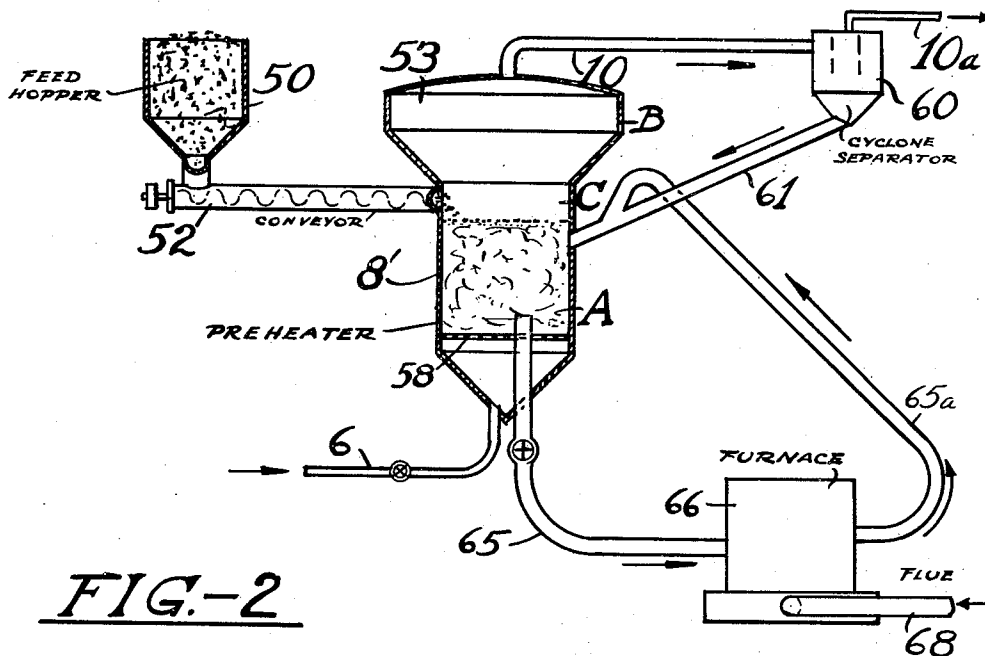
C. E. HEMMINGER

2,397,485

CHEMICAL PROCESS

Filed July 5, 1941

2 Sheets-Sheet 1



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CHEMICAL PROCESS

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2 Sheets-Sheet 2

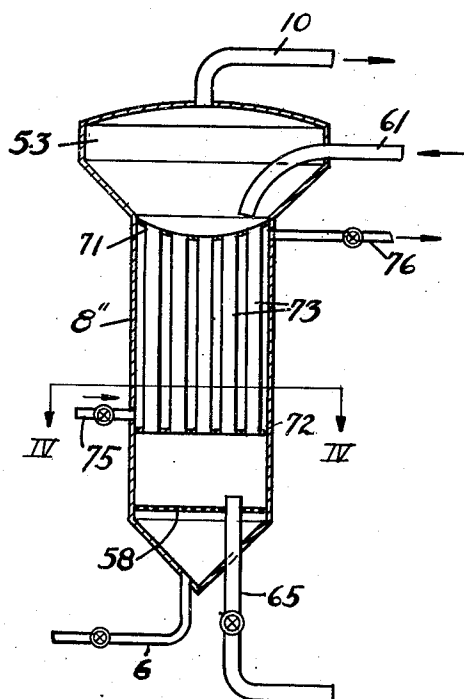


FIG-3.

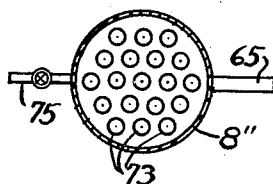


FIG-4.

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UNITED STATES PATENT OFFICE

2,397,485

CHEMICAL PROCESS

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Application July 5, 1941, Serial No. 401,184

3 Claims. (Cl. 196—52)

The present invention relates to the art of controlling chemical reactions, and in particular it relates to the art of transferring heat by means of a catalytic or inert solid material, such as granulated or powdered refractory material, from a preheating zone to a reaction zone.

As is well known in the chemical art, a great many commercial operations involve the application of heat. For best heat economy, it is often necessary to transfer sensible heat from one stage of a process to some other stage. In general this may be accomplished by heat exchange apparatus. The cost of heat exchange equipment ordinarily is relatively high, and the maintenance cost is also high, particularly where the chemicals undergoing reactions are of a corrosive nature and contact metallic heat transfer tubes. Thus in cases where acids or acid reacting substances are preheated in a heat exchanger, particularly where steam or moisture, together with air, are present, the reactant often causes excessive corrosion of metallic tubes or other surfaces with which it contacts. Another objection to heat exchangers is that it is often necessary to use large heat exchange surfaces due to the fact that only a limited distance between surfaces is allowable, and usually the velocity of fluids contacting the heat transfer surfaces is low.

My present invention relates to a method of controlling chemical reactions by the use of a solid, preferably in granular or powder form and disposed in a preheater or other vessel separate and apart from the reactor itself.

The main advantage of my present invention is that I secure better temperature control in chemical reactions by direct heat transfer from a solid to a vapor.

My present invention will be best understood by reference to the accompanying drawings which show diagrammatically in Figure 1 a modification of my invention in which the preheater consists of a case containing trays of heat transfer material, and Figures 2 to 4 represent modifications in which the heat transfer medium is in powdered form. Similar reference characters refer to similar parts throughout the several views.

Referring to Figure 1, a fluid reactant is introduced into the system through line 1 and thence discharged into a coil 3 located in a furnace 5. We may assume, for purposes of illustration, that the reactant is a gas oil and that the main reaction involved is one of cracking the gas oil catalytically to form hydrocarbons boiling within the gasoline range. This particular reaction

under known operating conditions, results in a conversion of gas oil to gasoline in amounts approximating 40% conversion of the charging oil to gasoline.

5 The oil is heated in coil 3 to vaporization temperatures and then withdrawn through a conduit 6 carrying a control valve 7 and discharged into the bottom of a preheater 8 containing a solid substance in the form of lumps, granules, pills, and the like. The solid material may be ceramic material, ordinary lime, iron or other metal balls, coke, sand, brick dust, slag or the like. The said material is non-catalytic with respect to the main reaction of the process. The solid material in the form of pills, balls, granules, etc., may be disposed on perforated trays 9 located within the preheater, and the passage of the vapors through the preheater results in a superheating of the said vapors by the solid material which is at a temperature of say 900° to 1150° F. or higher, and substantially higher than the incoming vapors. The vapors may be withdrawn through line 10 and thence delivered to a cracking zone 12 containing a stationary catalyst. The vapors in line 10 which were preheated in preheater 8 to cracking temperatures, say at temperatures from 825° to 925° F., upon contact with the catalyst which may be an acid treated clay such as "Super Filtrol," in reactor 12, undergo the desired conversion. The reaction products are withdrawn through line 14, condensed and recovered, in known manner, to obtain a quantity of gasoline.

When the reaction has proceeded in reactor 12 to the point where, as a result of the cracking, the catalyst becomes contaminated, it is necessary to discontinue the cracking reaction and to regenerate the said catalyst. This is accomplished by closing valves 7 and 11 to discontinue the flow of oil vapors to the preheater and the reactor and by opening a valve 16 in line 18, which line contains a regeneration gas, that is, a gas containing free oxygen, such as air, or air diluted with flue gas. If desired, after closing valve 7, and before discharging regeneration gas into the reactor 12, steam at 1000° F. or thereabouts may be discharged for several minutes into the said reactor to purge the catalyst of volatile hydrocarbons and the purging gas and hydrocarbons are withdrawn through line 14.

The purging operation is well known in the art and any inert gas such as steam, CO₂, N₂, or the like may be used. Thereafter the regeneration gas admitted through line 18 under known conditions of temperature and pressure, passes

upwardly through the reactor 12 and causes combustion of the contaminating deposits in reactor 12, whereupon the contaminants are converted to gaseous products of combustion and, mixed with the inert portions of the regeneration gas, are withdrawn as a flue gas through line 25. The effluent gases in line 25 may, and often do, contain combustibles such as CO, hydrogen, and normally gaseous hydrocarbons in more or less substantial amounts, that is to say, there may be about 2% volumetrically, each, of hydrogen, methane, CO, etc. Hence, it is advisable from the standpoint of economy, to discharge these flue gases into a combustion zone 26, together with oxygen or air added through line 28 and to cause the combustion of the combustible portion of the flue gases in said combustion chamber. The combustion of flue gases in chamber 26, of course further increases the heat content of the gases, and the gases thus further heated may be withdrawn through line 30 and thence passed into preheater 8 where they release at least a portion of their sensible heat to the solid material therein. The temperature of the gases in line 25 may be as high as 1050° F. to 1100° F., and the temperature of the gases in line 30 discharged into the preheater 8 may be as high as 1200° F. to 1400° F. The regeneration flue gases are withdrawn from the preheater through pipe 17 and may be used as a purging gas in the reactor, a diluent for the regeneration gas in line 18 or rejected from the system.

In Figure 2, I have shown a modified flow-plan illustrating an adaptation of my invention to accommodate the use of a powdered or otherwise finely divided solid in the preheater which is designated 8' in this modification.

As in the form shown in Figure 1, the vapors are contained in line 6 and are discharged into the preheater 8' which is constructed in such a form that the lower portion A is of smaller diameter than upper portion B, which latter section is a separation zone, as will more fully appear. Within 8' there is continuously maintained a body of solid inert material, such as sand, ground brick, lime, or any inert material finely divided so that it has a particle size of from 200-400 mesh. This material is maintained in a sort of heavy suspension within the portion A of reactor 8' by the upward flow of the vapors and the presence of a grid plate 58 containing orifices through which the gases flow.

The linear velocity of the gases is such that the suspension has a density of from 5 to 30 pounds per cubic foot under operating conditions, with a density of 10-12 pounds per cubic foot preferred. In the upper portion B of the preheater the gas velocities are from $\frac{1}{10}$ to $\frac{1}{2}$ those in section A and entrained powdered material gravitates from B into section A of the preheater. However, some fines may unavoidably be carried with the vapors in line 10 and, if so, these may be removed in a cyclone separator 60, or other suitable separating devices such as a Cottrell precipitator, and returned through line 61 to the preheater 8' or eliminated from the system.

Means are provided for feeding powdered material to the upper portion of section A, from a feed hopper 50 by a screw conveyor 52, projecting into the section. Ordinarily this source is employed only to start the operation or to make up for material lost, since a body of the powdered material, remains continuously in the

preheater in the form of a dense suspension having an upper level maintained at say C. Above C in section B the concentration of powdered material is very small. Of course, if the powdered material in section A of preheater 8' is at a temperature of 1000-1200° F. at the beginning of an operation, and the vapors in line 6 are at a temperature of 400-600° F., the powdered material in the preheater is sufficiently cooled so that it can no longer supply heat to the incoming oil vapors. It is necessary, therefore, to withdraw powdered material from the preheater 8 through line 65 and reheat it in a furnace 66, which may be similar in construction to preheater 8', or other suitable heating device. A convenient method of supplying the heat for reheating the material in 66 is to employ the flue gases resulting from regeneration of the catalyst, as hereinbefore indicated, or hot gases from exothermic reactions in the reactor 12.

In the modifications shown in Figures 3 and 4, the difference between this modification and that shown in Figure 2 resides solely in the structure of preheater 8'' as compared with 8'. The preheater 8'' contains tube sheets 71 and 72 between which extend a bank of spaced tubes 73. The upper tube sheet 71 is concave so that powdered material returning from 53 is directed into the tubes 73. If desired, a heat supplying fluid such as molten salts, mercury, etc., may be pumped through valved inlet pipe 75 and withdrawn through pipe 76. The bulk of the solid heat transfer material is maintained in a dense phase say having a density of 5 to 30 lbs. per cubic foot in tubes 73 or at least above grid plate 58. As in Figure 2, the solid material may be withdrawn through pipe 65, reheated in a furnace such as 66 and returned through pipe 61.

In the modifications shown in Figures 2 to 4, due to the presence of the solid material in the preheaters 8' and 8'', there is a more efficient lateral heat transfer to the metal walls than if there were no solid material. In other words, the coefficient of heat conductivity from the interior of 8' or 8'' to the metal walls of the preheater or the tubes in 8' or 8'' is greatly increased by the presence of the solid material over what it is where only gas or vapors are in the preheater. This device may also be used for cooling of gases where the medium about the tubes is cooler than the gas.

To recapitulate briefly, my present invention relates to improvements in the art of endothermic reactions or exothermic reactions in which it is necessary to preheat vapors passing to a reaction zone, and in its essence the inventive concept involves preheating the vapors or gases by direct contact with a hot finely divided material. The process involves the further thought of supplying heat to the preheating powder from extraneous added fuel or from some other stage of the complete process as, for example, where the main process involved is the cracking of gas oil in the presence of a catalytic material such as acid treated clay, which catalyst requires regeneration and which regeneration is usually accomplished by causing combustion of the carbonaceous material with the development of considerable heat and employing at least a portion of this latter heat to heat the powdered material in the preheater.

In cases where the reaction is exothermic such as oxidation reactions, the medium used to reheat the powder in chamber 66 of Figure 2 can be the heated gases from the reactor. Also, in

some endothermic reactions it may be desirable to place a furnace in line 10 so that the vapors leaving 8 are cooler than when leaving reactor 12. Then, the solid may be reheated in reheater 66 by these hot vapors and the waste sensible heat from the reactor can be used. This is important where there is no carbon deposit to be burnt to recover heat.

Also, heater 5 can be dispensed with and the liquid can be vaporized by spraying directly on the preheating material. Thus, any contaminant as ash or solid material in the liquid is removed on the solid material which can be removed from time to time or even be regenerated itself. Thus, the preheating solid may be catalytic to remove sulfur from gas oils and the preheating in 66 may be an oxidation zone where the sulfur is burnt off.

My process obviously has many adaptations other than those specifically mentioned, and it is to be understood that the specific details given herein are purely illustrative and do not impose any limitation on my invention.

What I claim is:

1. The process of cracking hydrocarbon oils which comprises vaporizing the said oils, conducting the oil vapors to a zone containing a dense suspension of powdered inert material,

which powdered material is at a higher temperature than the entering vapors, separating the major portion of the inert material from the oil vapors and conducting the oil vapors to a reaction zone where they contact a catalyst adapted to effect the desired conversion.

2. A process of catalytically cracking hydrocarbon oil which comprises passing hot oil vapors to a preheating zone containing a dense suspension of powdered inert material at a higher temperature than the entering vapors, separating most of the powdered material from the oil vapors leaving said preheating zone, conducting the preheated oil vapors to a reaction zone where they contact a catalyst for cracking the vapors, and supplying heat to the powdered inert material in said preheating zone.

3. The process of cracking hydrocarbon oils which comprises spraying the said oils into a zone containing a dense suspension of powdered inert material, which powdered material is at a higher temperature than the entering vapors, separating the major portion of the inert material from the oil vapors and conducting the oil vapors to a reaction zone where they contact a catalyst adapted to effect the desired conversion.

CHARLES E. HEMMINGER.