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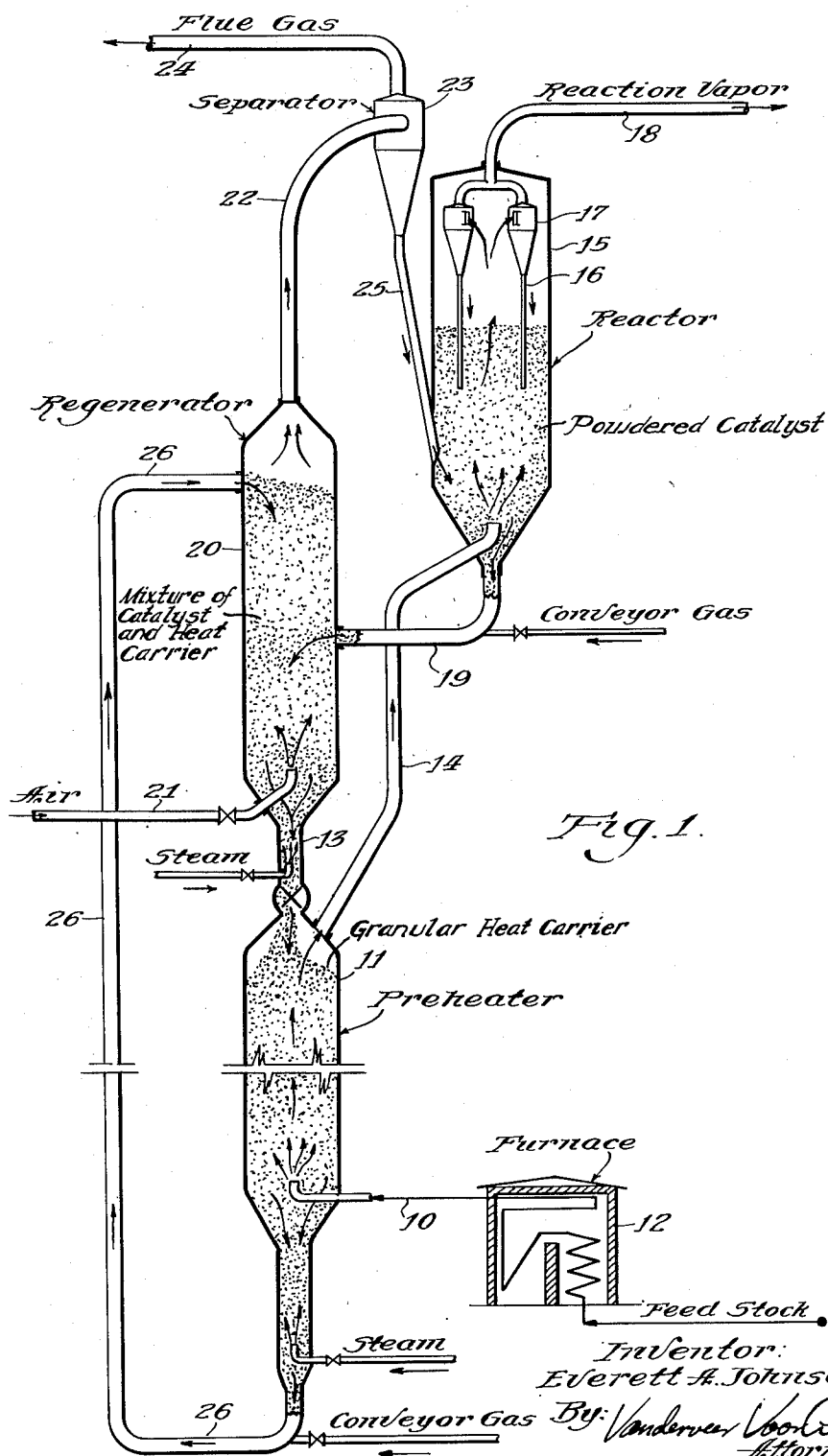
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CONVERSION OF HYDROCARBONS WITH SUSPENDED CATALYSTS

Filed Aug. 27, 1941

2 Sheets-Sheet 1



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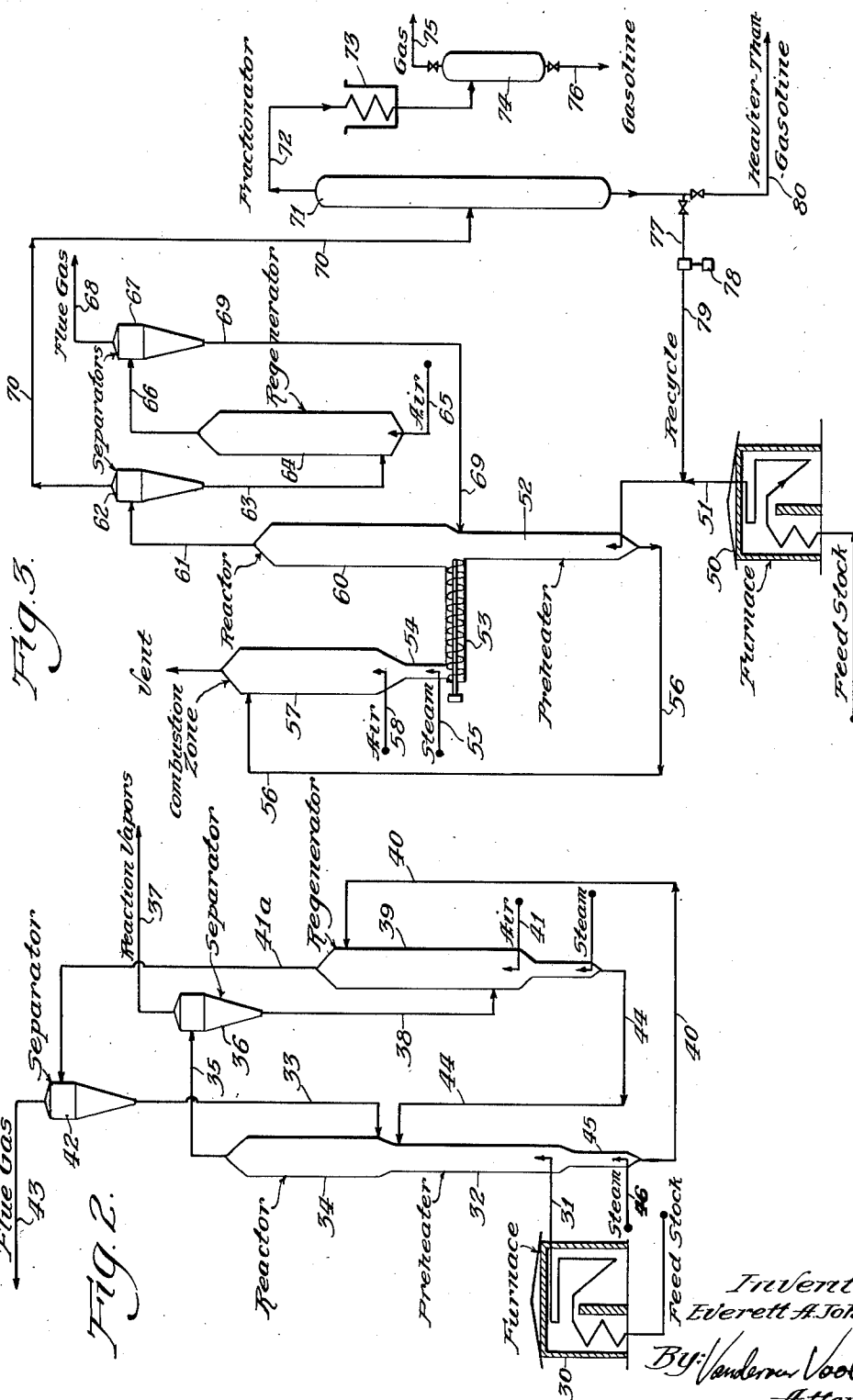
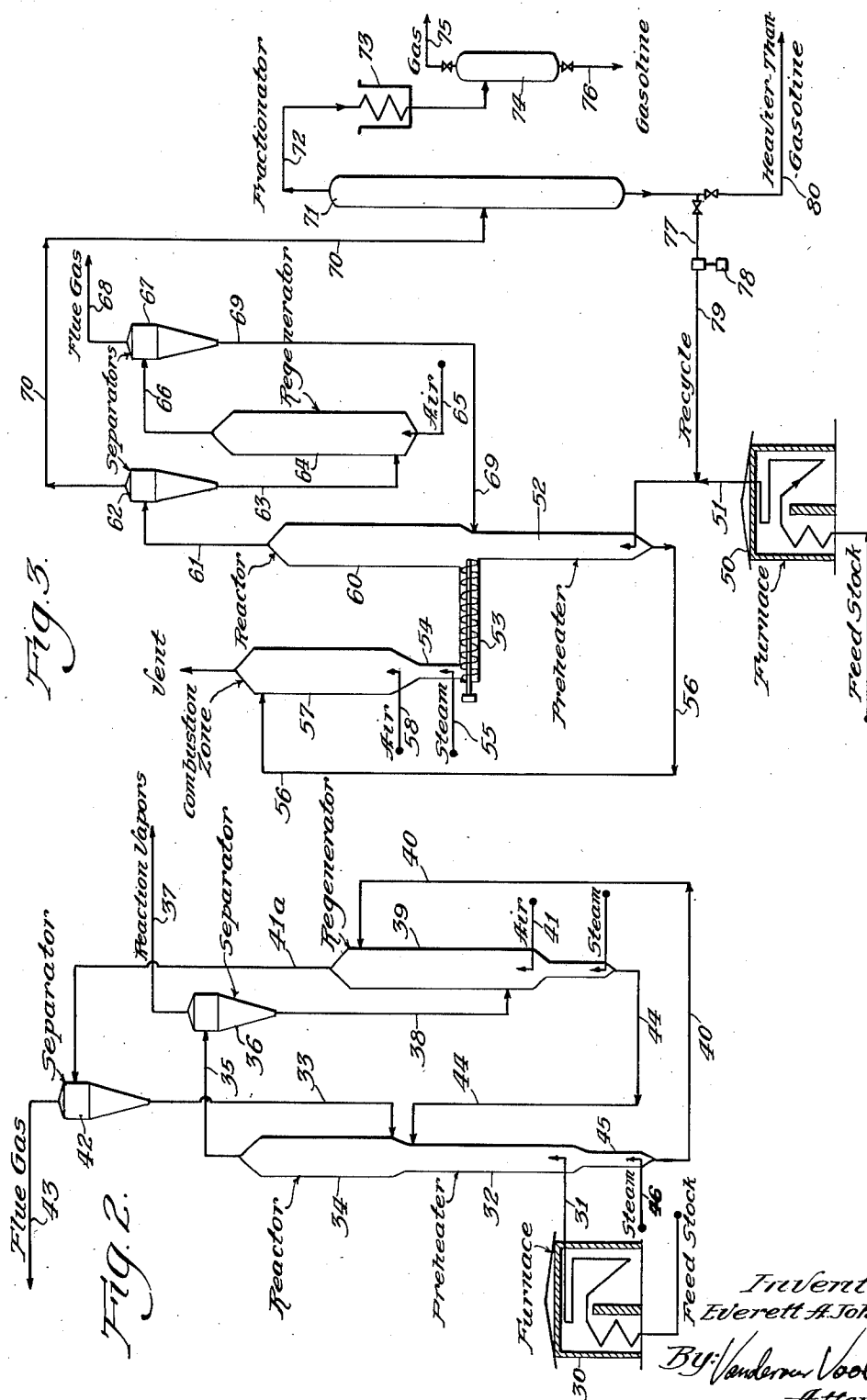
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2 Sheets-Sheet 2



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CONVERSION OF HYDROCARBONS WITH
SUSPENDED CATALYSTSEverett A. Johnson, Park Ridge, Ill., assignor to
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15 Claims. (Cl. 196—52)

This invention relates to the conversion of hydrocarbons and more particularly to the conversion of hydrocarbon oils in the presence of catalysts wherein heavy hydrocarbon oils are cracked to produce high knock rating gasoline. The invention relates especially to methods and apparatus for handling dirty stocks and incompletely volatile oils such as petroleum residues in a catalytic conversion process.

One object of the invention is to effect the conversion of dirty stocks without difficulties from excessive catalyst contamination. Another object is to effect the vaporization of dirty stocks without difficulties from carbon deposition in heating coils, etc. Another object of the invention is to obtain a maximum yield of gasoline of high knock rating from petroleum residues and petroleum cycle stocks. Still another object of the invention is to utilize to a large extent heat available in the catalytic conversion process resulting from the combustion of carbonaceous matter deposited on the catalyst, thereby reducing the fuel requirements of the process and increasing the overall operating economy. Other and more detailed objects, uses and advantages of my invention will become apparent as the description thereof proceeds.

The invention is illustrated by the accompanying drawings in which:

Figure 1 shows an apparatus in which the charging stock is vaporized in a preheater and the vapors are converted under the action of the catalyst in a separate reactor;

Figure 2 shows a similar apparatus in which the reactor and the preheater are combined in a single tower; and

Figure 3 shows in diagrammatic form an apparatus in which the heat required for the preheater is developed in a combustion zone separate from the regenerator employed for regenerating the catalyst.

Referring to Figure 1 of the drawings, the charging oil is introduced by line 10 into preheater 11. The oil may be a typical gas oil charging stock having a wide boiling range, for example, between 500 and 760° F., or it may be an incompletely volatile residual oil remaining from the topping of crude petroleum. Tar from thermal cracking operations and other unvaporizable hydrocarbon oils difficult to process in ordinary cracking processes may likewise be employed. The charging stock may be partially heated in furnace 12 or in suitable heat exchangers not shown. In the case of gas oil, the charging stock may be completely vaporized in

furnace 12 before introducing it into the preheater. The oil may also be sprayed into the preheater 11 in liquid form and completely vaporized therein.

Preheater 11 is supplied with a granular, refractory, solid heat carrier which may be introduced by line 13. This material may be relatively coarse, for example, $\frac{1}{2}$ or $\frac{1}{4}$ inch down to 50 or 100 mesh. In the preheater it is maintained in a turbulent, dispersed condition by the action of the upflowing oil vapors passing through the preheater. The oil charged, which may have been preheated in heater 12, for instance, to a temperature of 500 to 800° F., is then further heated in the preheater 11 where the temperature is still further increased by contact with the hot, solid, granular material which is supplied to the preheater at an elevated temperature, e. g., 1000 to 1500° F. Contact with the granular heat carrier in 11 results in the complete vaporization of the vaporizable ingredients of the oil when introduced in the liquid form. Non-vaporizable ingredients in the feed stock are deposited on the heat carrier material and then substantially converted to coke or carbon.

The heat carrier material employed in preheater 11 may suitably be crushed firebrick, sand, subdivided metal, for example, iron shot, aluminum pellets or other granular or preformed, e. g., pilled, refractory material, preferably a refractory metal oxide. Coke deposited on heat carrier material is removed by oxidation as hereinafter described. An important characteristic of the heat carrier material is that it has a settling rate higher than that of the catalyst being employed. The rate of settling is determined by the size, shape and density of particles, and I select a heat carrier whose particles, through greater size, more compact shape and/or greater density, fall more rapidly through the gaseous medium than do the particles of catalyst. Consequently, when dispersed in an upflowing vapor stream having the proper velocity intermediate the settling rate of the catalyst and the heat carrier, the former is buoyed up and separated rapidly from the latter which falls through the vapor stream.

At the top of tower 11 the hydrocarbon vapors are withdrawn by line 14 leading to reactor 15 provided with a cone bottom for catalyst settling therein. It is preferred that the catalyst be maintained in the reactor in the dense phase, i. e., about 15 to 25 pounds of catalyst per cubic foot. The dense phase of the catalyst is maintained to a large extent by returning it to the

reactor 15 through catalyst legs 16 leading from catalyst separator 17. Vapors substantially freed of catalyst pass from the reactor by line 18 leading to a fractionating column not shown.

The catalyst is withdrawn from the reactor 15 by line 19 leading to regenerator 20. In regenerator 20 the temperature is maintained sufficiently high to insure rapid oxidation of carbonaceous material on the catalyst. Air or other oxygen-containing gas for this purpose is admitted by line 21 and the spent regeneration gases pass by line 22 into cyclone separator 23. Spent regeneration gases from separator 23 are discharged from the system by line 24 while the regenerated catalyst is recovered in separator 23 and conducted by line 25 back to reactor 15, substantially without cooling.

From the base of preheater 11 the granular heat carrier is conducted by line 26 to the upper part of regenerator 20 whence the material descends through the regenerator in contact with a slow stream of air introduced by line 21. A mixture of granular heat carrier material and catalyst, in which the heat carrier predominates, is withdrawn from regenerator 20 by line 13 and conducted back to the preheater 11. The temperature of the heat carrier material recycled through the preheater in this way is ordinarily about 1000° F., preferably about 1200° F. The amount is sufficient to provide a substantial part of the heat for the charging stock in preheater 11 and to insure vaporization of this stock, thereby eliminating from the reactor those hydrocarbons having a tendency to deposit large amounts of carbon on the catalyst.

Referring now to Figure 2, the oil is heated and/or vaporized in furnace 30 and passed by line 31 into the combined preheater 32 and reactor 34. The vapors or oil are first heated or vaporized by solid, granular material in said preheater. After the vapors pass upwardly they come in contact with finely divided catalyst introduced by line 33 at an intermediate point in said preheater-reactor. The catalyst remains suspended in the hydrocarbon vapors in the reaction zone 34 in the upper part of said reactor-preheater and the products, including catalyst, are transferred from 34 by line 35 to cyclone separator 36 wherein the catalyst is separated from the vaporous products which are withdrawn by line 37.

From the base of cyclone separator 36 the catalyst is withdrawn by line 38 leading to regenerator 39. Simultaneously, the heat carrier material is withdrawn from the base of preheater 32 and conducted by line 40 to the upper part of regenerator 39. Air or other oxygen-containing gas is introduced into regenerator 39 by line 41, thereby supplying oxygen for the combustion of carbonaceous matter deposited on the catalyst.

The fine catalyst material is carried upwardly with the regeneration gases through regenerator 39 and thence by line 41a to separator 42 whence the gases escape by line 43 and the regenerated catalyst is conducted by line 33 back to reaction zone 34. The granular heat carrier is conducted by line 44 to an intermediate point in the preheater-reactor, the hot, heat carrier substance serving to evaporate the heavy hydrocarbons as herein previously described. In order to avoid passage of hydrocarbon vapors from the preheater, with the heat carrier through line 40 leading to regenerator 39, I may pass the catalyst first through a short stripping section 45 at the base of the preheater. A small amount of steam ad-

mitted by line 46 will serve to prevent the passage of hydrocarbon gases with the catalyst into the regenerator 39.

Another embodiment of the invention is illustrated by Figure 3 as follows: Oil is charged to furnace 50 where it is heated and conducted by line 51 to preheater 52 containing a suitable heat carrier material as previously described. The stock is evaporated by contacting with the hot heat carrier introduced through feeder 53 from stripping section 54 supplied with stripping steam from line 55. In passing through preheater 52 the heat carrier becomes substantially cooled and also coated with carbonaceous deposit. The spent heat carrier is withdrawn by line 56 leading to the upper part of combustion zone 57 where the carbonaceous material is burned from the carrier by air or oxygen introduced by line 58.

Preheated products from 52 are passed upward into reactor section 60 where they are brought into contact with a suitable suspended catalyst hereinafter described in greater detail. Due to its greater buoyancy, the catalyst is carried upward through the reactor while the heat carrier settles through the preheater 52 and is recycled to combustion zone 57. The catalyst and reaction products pass from the reactor by line 61 to separator 62 from which the catalyst is withdrawn by line 63 leading to regenerator 64. A controlled stream of air or other oxygen-containing gas supplied by line 65 effects regeneration of the catalyst held in suspension in chamber 64. The catalyst and regeneration gases are transferred by line 66 to cyclone separator 67 from which the spent regeneration gases are discharged by line 68 and the regenerated catalyst is withdrawn by line 69 leading back to reactor 60.

Products from separator 62 flow by vapor line 70 to fractionator 71 where they are fractionated into a light gasoline overhead fraction and heavy cycle stock. The overhead fraction flows by line 72 to condenser 73 and receiver 74 from which gases are vented by line 75 and the gasoline product is withdrawn by line 76. The heavier than gasoline products are withdrawn from the base of fractionator 71 by line 77 and pump 78 and are thence returned by line 79 to preheater 52 for vaporization and further conversion. Part or all of the heavier than gasoline product fractions may be discharged from the system by valved line 80.

In operating my process I prefer to employ catalysts of the siliceous type, such as acid treated clays, bentonite, etc. I may also employ active silica, silica gel, etc., generally associated with alumina or magnesia in amounts of 15 to 30% of the latter. Silica gel or precipitated silica intimately associated with about 2 to 5% of alumina and zirconia is a satisfactory catalyst. I prefer to employ the catalyst in the form of fine granules, for example, particles of the order of 100 to 400 mesh screen size or finer. Multiple cyclone separators of small diameter and high efficiency may be used for recovering the catalyst from the product vapors and/or regeneration gases. I may also employ electrical precipitators for this purpose or suitable scrubbing devices. For example, I may scrub the spent regeneration gases or the product vapors with feed stock which is subsequently charged to the process directly to the preheater and any catalyst which has collected in the oil may thus be returned to the system.

I prefer to regulate the amount of catalyst in the system to about 1 to 20 parts of catalyst by weight in the reactor per volume of oil charged

to the system per hour. Thus a unit with a capacity of 1000 pounds of oil per hour would retain about 1000 to 20,000 pounds of catalyst in suspension in the reactor. The catalyst life will ordinarily be from 20 minutes to 2 hours, depending on the character of the stock being treated and other factors. In my process of preconditioning the feed stock by contacting with a hot heat carrier substance, thereby eliminating from the stock certain carbon forming substances, I obtain a lower rate of carbon deposition than ordinarily obtained in catalytic cracking operations and consequently I am enabled to increase the life of the catalyst in the reactor. It will be understood that, although the heat carrier material may be essentially non-porous and without catalytic activity of itself, it carries a film of catalyst on the surface which promotes decomposition of those constituents of the feed stock which break up readily to form carbon. Heat carriers having a mild catalytic effect may also be used if they meet the other requirements of high heat capacity and ruggedness.

The temperature of operation employed in my process will usually be about 875 to 1025° F. in the reaction zone and somewhat higher than this in the preheater, a range of 800 to 1050° F. including substantially all conditions. I prefer passing the hydrocarbon vapors immediately from the preheating or preconditioning zone to the reaction zone, in order to avoid any fall in temperature therebetween and this may be best accomplished in an apparatus like that shown in Figure 2, where the preheating zone and reaction zone occupy the lower and upper parts of the same chamber. Heat carrier material being coarse and of greater density than the catalyst, occupies the lower or preheating section while the conversion catalyst being finer and more readily suspended in the vapors occupies the upper part of the chamber, thereby avoiding any loss of heat between the preheater and the reactor. It is desirable, of course, to control the upward average velocity of the vapors to permit the heat carrier to fall while maintaining the catalyst in suspension.

The pressures employed in my process are generally low, e. g., atmospheric to 50 pounds per square inch gage. Pressures of 5 to 20 pounds per square inch may commonly be employed. The use of higher pressures, of the order of 100 pounds per square inch, introduces certain difficulties in controlling the handling of the various materials in the process.

In that modification of my process shown in Figures 1 and 2 wherein the heat carrier circulates from the preheater to the catalyst regenerator, the heat carrier material is heated in the regenerator by the combustion of carbonaceous matter from the catalyst. In this way the heat carrier serves to control the temperature of regeneration, an essential of the process. It is desirable that the catalyst regeneration temperature be maintained with the range of about 1000 to 1400° F., although temperatures as high as 1600° F. may be used with certain more thermally stable catalysts. Ordinarily, a regeneration temperature of 1100 to 1200° F. is most satisfactory. The rate of recycling the heat carrier to the regenerator may be employed to control the temperature of that operation. Flexibility of operation of the process is best obtained by regulating the temperature of the oil and the hydrocarbon vapors supplied to the preheater, i. e., sufficient heat may be introduced into the feed stock

to balance the heat requirement of the process when maintaining the desired regeneration temperature by recycling the heat carrier between the regenerator and the preheater.

In that modification of my process shown in Figure 3 wherein the heat carrier material is recycled to a separate combustion zone rather than to a catalyst regenerating zone, the heat in the combustion zone may be regulated by either the amount of carbon deposited on the heat carrier in the preheater or by the amount of air or other oxygen-containing gas introduced into the combustion zone. Thus, when charging highly carbonaceous, incompletely volatile tars and crude residuums to the vaporizer or preheater, the amount of carbon deposited on the heat carrier will be sufficient to provide more heat on combustion than is desired in the preheater. In that case, I may limit the extent of combustion in the combustion zone by incompletely burning off the carbonaceous deposit or I may reduce the proportion of residuum or tar employed in the feed stock and substitute for it clean vaporizing feed stock such as virgin gas oil or recycle oil obtained in the process.

Although I have described my invention with respect to specific embodiments thereof, I intend that it be limited only by the scope of the following claims. Thus, where I have described downward flow of heat carrier through the preheating zone, I may make the heat carrier flow in suspension upward and out through an overflow located in a relatively quiescent zone near the top of the preheating zone. Other modifications of my invention will be obvious to those skilled in the art. I claim:

1. The process of converting heavy hydrocarbon oil into gasoline motor fuel which comprises introducing a heavy hydrocarbon oil into a heating and vaporizing zone, heating the vapors of said oil in said zone to the desired conversion temperature by contacting therein with a hot, granular inert, refractory heat carrier material maintained in turbulent dispersion in said vapors, thereby depositing on said heat carrier, carbonaceous material resulting from the deposition and vaporization of said heavy hydrocarbon oil, separating the vapors of said hydrocarbon oil from said heat carrier and transferring them at conversion temperature to a reaction zone wherein they are contacted with a solid, porous, conversion catalyst maintained in suspension in said vapors, separating the reaction products from said catalyst, regenerating said catalyst by suspending it in an oxygen containing gas under controlled temperature conditions and restoring the temperature of said heat carrier material by combustion of said carbonaceous material therefrom under controlled temperature conditions.

2. The process of converting hydrocarbon oil which comprises vaporizing said oil and heating the vapors to a high conversion temperature in a turbulent heating zone containing a hot, dispersed, solid inert heat carrier material maintained in turbulent dispersion in said heating zone, said heating being predominantly by the action of said material, separating hot vapors from said heat carrier material and contacting them at said high conversion temperature in a reaction zone with a turbulent suspended, subdivided, solid, conversion catalyst wherein the oil vapors are converted substantially to high knock rating gasoline and the catalyst is contaminated with a carbonaceous deposit, separating the hy-

drocarbon vapors from the catalyst, regenerating the catalyst by controlled combustion in a regenerating zone in the presence of said granular, refractory heat carrier material which is heated by the exothermic heat of regeneration in said regeneration zone, transferring said hot heat carrier material to said heating zone first mentioned, contacting it therein with the hydrocarbon oil charged to the process and then recycling it to said regeneration zone.

3. The process of claim 2 wherein said heating zone lies below said reaction zone in substantially unrestricted communication therewith.

4. The process of claim 2 wherein the heat carrier material is heated to a temperature between about 1000 and 1600° F. in said regeneration zone before it is transferred to said heating zone.

5. The process of claim 2 wherein the heat carrier material cooled in said heating zone by transfer of heat to said oil vapors is recycled to said regeneration zone at a rate sufficient to control the temperature of said regeneration zone within a range of about 1000 to 1400° F.

6. In the process of converting heavy hydrocarbon oil to gasoline wherein the vapors thereof are contacted in a reaction zone with a solid, hydrocarbon, conversion catalyst at a conversion temperature in the range of about 800 to 1050° F., the reaction products are separated from the catalyst and the catalyst is periodically regenerated by controlled combustion in a regeneration zone to remove carbonaceous matter deposited thereon, the improvement comprising initially contacting the vapors of said hydrocarbon oil in a vapor heating zone with a hot granular, refractory, solid inert heat carrier material, whereby there is adsorbed on said heat carrier material carbonaceous matter which would otherwise be deposited on said catalyst, separating heat carrier material from heated hydrocarbon vapors and conducting the hot vapors to said reaction zone, and recycling said heat carrier material between said vapor heating zone and a combustion zone where said carbonaceous matter is removed by controlled combustion and the temperature of the heat carrier material is restored before returning to said heating zone.

7. The process of claim 6 wherein the reaction products are fractionated to remove gasoline therefrom and heavier products are recycled to said heating zone.

8. The process of claim 6 wherein at least part of the heavy hydrocarbon oil charging stock supplied to said operation is petroleum residuum in unvaporized form.

9. In the process of converting hydrocarbon oils into high knock rating gasoline wherein the hydrocarbon vapors are contacted at conversion temperature with a suspended, finely divided, solid, conversion catalyst in a conversion zone, the vapors are separated from the catalyst and the catalyst is regenerated by burning in a regeneration zone and recycled in the process, the improvement comprising initially conducting the hydrocarbons through a preheating section in the lower part of said conversion zone, wherein said hydrocarbons are heated to the desired conversion temperature, by contact with a hot, granular heat carrier material, maintaining said material in suspension in the hydrocarbon vapors therein, withdrawing said heat carrier material at a lower temperature from said preheating section, reheating said heat carrier material by dispersing it in said regeneration zone in intimate contact with catalyst therein, whereby the tem-

perature of said heat carrier material is restored by the heat of regeneration of catalyst, separating hot heat carrier material from catalyst and recycling it to said preheating section in the base of said conversion zone.

10. In the process of converting hydrocarbons by contacting hydrocarbon vapors with a suspended, finely divided, solid catalyst in a reaction zone, separating the catalyst from reaction products, regenerating the catalyst by controlled combustion in a regeneration zone, and recycling the catalyst in the system, the improvement comprising introducing into said regeneration zone granular heat carrier material having a higher rate of settling than that of said catalyst, absorbing part of the exothermic heat of regeneration in said heat carrier material, conveying said catalyst and said heat carrier material in admixture to a preheating zone and passing the vapors of said hydrocarbons upwardly through said preheating zone and thence to said reaction zone, the velocity of the vapors in said preheating zone being sufficiently high to carry away the catalyst in suspension to the reaction zone but sufficiently low to allow said heat carrier material to settle therethrough and recycling said heat carrier material to said regeneration zone.

11. In the process of converting hydrocarbons with solid refractory conversion catalysts wherein the catalyst, in finely divided form, is suspended in a continuous stream of hydrocarbon vapors at conversion temperature and the catalyst is subsequently separated from the hydrocarbon products, regenerated by combustion with an oxygen-containing gas to remove from the catalyst carbonaceous deposits which impair its activity and the regenerated catalyst is returned to the hydrocarbon contacting step, the improvement comprising preheating hydrocarbons before contacting with said catalyst by contact with a hot, dispersed, granular, refractory heat carrier material in a pre-heating zone, transferring partially cooled heat carrier material from said preheating zone to a regeneration zone, commingling catalyst and heat carrier material in said regeneration zone, supplying oxygen-containing gas to said regeneration zone, thereby restoring the activity of the catalyst and restoring the temperature of said heat carrier material, separating heat carrier material from the catalyst and returning it while hot to said preheating zone, returning the separated catalyst to a reaction zone wherein it is contacted with preheated hydrocarbons from said preheating zone and thence conducting spent catalyst back to said regeneration zone.

12. The process of claim 11 wherein separation of heat carrier material and catalyst is effected within said regeneration zone by the classifying action of the regeneration gases, said gases carrying away said catalyst particles in suspension to a separation zone wherein catalyst is separated from regeneration gases and discharged to said reaction zone.

13. An apparatus for converting hydrocarbon oil by contacting with catalysts at conversion temperature which comprises an elongated, vertical tower, a heating chamber in the lower part of said tower, a reaction chamber in the upper part of said tower of larger cross-sectional area than said heating chamber and in direct communication therewith, means for introducing hydrocarbon charging stock into said heating chamber means for conducting catalyst from said reaction chamber to a regenerator, means for

supplying an oxygen-containing gas to said regenerator for burning carbonaceous material from said catalyst, means for withdrawing reaction products from said reaction chamber, means for introducing finely subdivided solid conversion catalyst intermediate said heating and reaction chamber, means for dispersing said catalyst in hydrocarbon vapors flowing from said heating chamber to said reaction chamber, means for recycling a hot, granular, inert, solid refractory heat carrier material thru said regenerator and thru said heating chamber in series to transfer heat from the former to the latter.

14. In the process of regenerating finely divided, solid catalyst by which contaminating carbonaceous material is removed by reaction with an oxidizing gas, accompanied by the generation of heat, the method of controlling the temperature of said regeneration reaction and avoiding the development of temperatures damaging to said catalyst which comprises introducing into said regeneration reaction a relatively cool, inert, solid, granular, heat-absorbing material, having a higher settling rate than that of said catalyst, intimately dispersing said heat-absorbing material in contact with the said catalyst undergoing regeneration whereby the temperature of the said heat-absorbing material is substantially increased, separating the hot heat-absorbing ma-

terial from the regenerated catalyst, cooling said heat-absorbing material by contact with a hydrocarbon stock having a tendency to deposit carbon on said inert heat-absorbing material and reintroducing said heat-absorbing material into said regeneration reaction.

15. In an exothermic gas phase reaction wherein a finely divided solid catalyst is contacted with reacting gases at an elevated temperature and the resulting heat of reaction tends to raise the temperature to a point of damaging the catalyst, the method of controlling the temperature of said exothermic reaction and avoiding the development of temperatures damaging to said catalyst which comprises introducing into said exothermic reaction a relatively cool, inert, solid, granular heat-absorbing material, having a higher settling rate than that of said catalyst, intimately dispersing said heat-absorbing material in contact with the said catalyst whereby the temperature of the said heat-absorbing material is substantially increased, separating the hot heat-absorbing material from the catalyst, cooling said heat-absorbing material by contact with a hydrocarbon stock having a tendency to deposit carbon on said inert heat-absorbing material and reintroducing it into said exothermic reaction.

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