

Nov. 15, 1949

L. P. EVANS

2,487,794

HYDROCARBON CONVERSION PROCESS

Filed Dec. 19, 1947

2 Sheets-Sheet 1

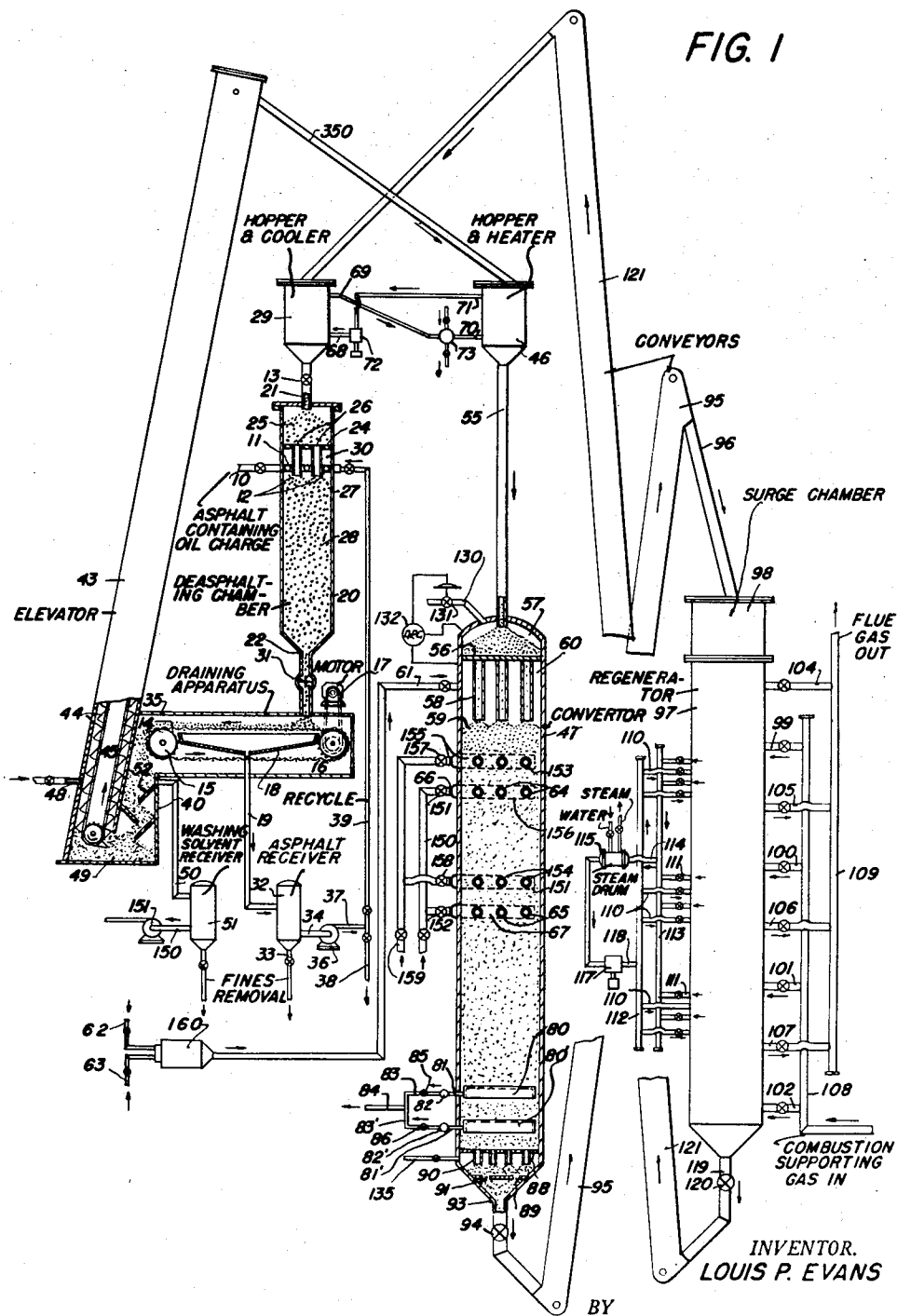


FIG. 1

INVENTOR.
LOUIS P. EVANS

BY

John A. Crowley, Jr.
AGENT OR ATTORNEY

Nov. 15, 1949

L. P. EVANS

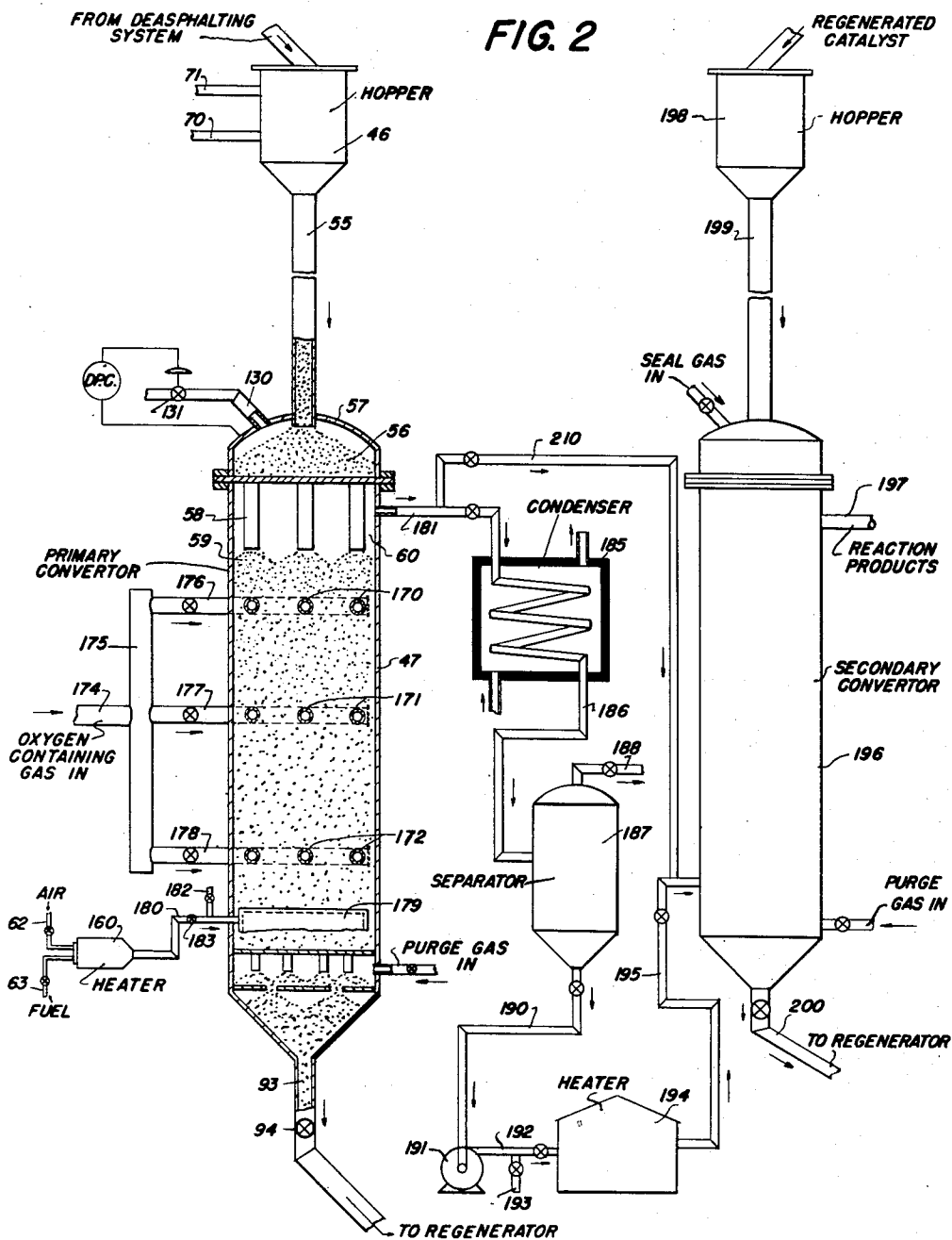
2,487,794

HYDROCARBON CONVERSION PROCESS

Filed Dec. 19, 1947

2 Sheets-Sheet 2

FIG. 2



INVENTOR.
LOUIS P. EVANS

BY
John A. Crowley, Jr.
AGENT OR ATTORNEY

UNITED STATES PATENT OFFICE

2,487,794

HYDROCARBON CONVERSION PROCESS

Louis P. Evans, Woodbury, N. J., assignor to Socony-Vacuum Oil Company, Incorporated, a corporation of New York

Application December 19, 1947, Serial No. 792,730

15 Claims. (Cl. 196—52)

1

This invention pertains to a process for conversion of high boiling hydrocarbons at controlled elevated temperatures in the presence of a particle-form contact mass material. This invention is particularly concerned with a process for the conversion and partial oxidation of hydrocarbon feed stocks which originally contain both asphaltic and oily constituents.

Such conversion processes may involve treating, polymerization, cracking, dehydrogenation, desulphurization, etc., usually accompanied by partial oxidation of some of the hydrocarbons. A particularly important process is the catalytic cracking conversion of hydrocarbons, it being well known, for example, that hydrocarbon fractions boiling above the gasoline boiling range may be converted to lower boiling gasoline containing hydrocarbons upon being subjected to contact with a suitable solid porous catalyst at temperatures of the order of 800° F. and upwards and at pressures usually above atmospheric. Another important process is the catalytic dehydrogenation of hydrocarbons usually occurring at temperatures of the order of 900°–1200° F.

Heretofore, such conversion processes have been limited to the conversion of relatively light, clean, substantially tar or asphalt free petroleum feed stocks because of the tendency of the asphalt containing stocks to cause the formation of excessive deposits of coky contaminants on the catalyst which deposits cannot be economically removed. In order to avoid these heavy coke deposits which render the cracking process unfeasible, it has been the wide refinery practice to subject some high boiling petroleum feed stocks (when available with a broad boiling range) to a preliminary tar separation step, separate an easily vaporizable fraction from a liquid fraction which bears the asphaltic constituents and to subject only the vaporizable fraction to catalytic cracking while discarding the liquid tar separator bottoms. Since this discarded fraction may be made up of a large proportion of valuable oily constituents and a smaller proportion of asphaltic constituents, it is obvious that a large quantity of otherwise acceptable catalytic cracking feed stock is lost and unavailable as such in the prior art tar separator operation. When the crude residuum is not of such boiling range and does not contain substantial amounts of vaporizable gas oil, it has been considered in practice as being unsuitable as such for a cracking charge stock. The problem is becoming increasingly serious due to the fact that relatively low boiling petroleum

2

crudes are becoming less plentiful and the crudes which are most readily available are high boiling crudes in which the oily constituents boil so high as to prevent their separation from asphaltic constituents by distillation process without subjecting them to temperatures at which undesirable thermal cracking and excessive coking occur. As a result, in order to use such high boiling stocks at all, it is necessary first to subject them to a preliminary thermal coking step to provide some lower boiling oily fractions for a subsequent catalytic cracking operation. By-products from the coking process are a heavy liquid cut which may contain a substantial amount of oily constituents as well as asphaltic constituents and a very large amount of petroleum coke, the disposal of which often creates a serious refinery problem.

A novel process for conversion of the oily constituents in asphalt bearing feed stocks which avoids the above difficulties is described and claimed broadly in my co-pending application Serial Number 720,271, now abandoned filed in the United States Patent Office January 4, 1947. In the process described in that application the hydrocarbon feed fraction bearing asphalt and oily constituents is contacted under suitable sorption conditions with a particle-form porous contact material which is suitable for sorbing the oily constituents of the feed in the pores of the contact material while leaving substantially unadsorbed the asphaltic constituents of the liquid feed. A substantial separation of unadsorbed asphaltic constituents from the contact material bearing sorbed oily constituents is then effected. The separated contact material bearing sorbed oily constituents is then heated to a temperature suitable for effecting the desired conversion of the sorbed oily constituents. The present invention is specifically directed to certain improvements in the above described process particularly in the step of heating the contact material bearing sorbed oily constituents and in effecting the conversion of said oily constituents to the desired products. According to a preferred form of this invention the contact material after having sorbed the oily constituents of the original asphalt bearing feed is heated in the absence of the separated asphalt constituents to a temperature suitable for the conversion of the sorbed oily constituents by the passage of a combustion supporting gas through the contact mass so as to partially oxidize some of the sorbed oily constituents and thereby release the required heat. The mixed conversion products are withdrawn

together and separated in conventional equipment.

A major object of this invention is the provision of a process for conversion of high boiling asphalt bearing hydrocarbon fractions which process avoids the above described difficulties of the prior art.

Another object is the provision of a practical method for catalytically converting the oily constituents in high boiling petroleum residuums without the formation of prohibitive amounts of coke during such conversion.

A specific object of this invention is the provision of a continuous cyclic process for conversion and partial oxidation at elevated temperatures of the oily constituents present in asphalt bearing hydrocarbon fractions.

Another specific object is the provision of an improved continuous process for catalytic conversion of the oily constituents in asphalt bearing hydrocarbon residuums and for the regeneration of the catalyst material involved.

These and other objects of this invention will become apparent from the following discussion.

It has long been known that when porous adsorbents such as bauxites and natural and treated clays are contacted with liquid petroleum fractions, the asphaltic constituents may be adsorbed on the clay and thus removed from the oily constituents. Such a process is commercially employed for the decolorizing of mineral oils by percolation of the oils through clay-type adsorbents. The present process is the opposite of the so-called percolation and contact filtration processes for oil refining in that, by the present process, it is the oily constituent and not the asphaltic constituent which is sorbed by the contact material. This fundamental difference makes possible the process of this invention and permits the elimination of the asphalt materials without contamination of the catalyst thereby. It has been found that porous contact materials, having a of low macropore volume with an average pore

units, should constitute less than about 30 percent of the total pore volume and preferably 10 percent or less. The measurement of pore size and pore size distribution in various porous materials is discussed in detail by L. C. Drake and H. L. Ritter in *Industrial and Engineering Chemistry, Analytical Edition*, volume 17, pages 782-791, 1945. The methods described there were essentially those employed in determining the bulk densities, average pore diameters, and other pore measurements of the adsorbents employed in the present invention.

The size of the sorbent particles employed in the process of this invention is to some extent dependent upon the variables involved in any particular application of the process. These important variables are time of contact between the liquid asphalt bearing charge and the sorbent in the sorption zone, temperature in the sorption zone, viscosity of the liquid charge, and to a lesser extent the ratio of liquid oil to sorbent charged to the sorption zone. Increasing time of contact and increasing temperature result in a decrease in the efficiency of separation of asphaltic and oily constituents. Decreasing viscosity of the liquid charge has the same effect. On the other hand increasing temperature and decreasing viscosity both result in more rapid sorption of the liquid oily constituents by the sorbent. If the ratio of sorbent to liquid charge is excessive some loss in separation efficiency results. By proper control of these variables some latitude in the average diameter of the sorbent employed may be provided. However, when the diameter of the particles becomes too small, the sorbent preferentially adsorbs the asphaltic constituents from the liquid charge in the same manner as well known oil filtering clays. This is shown in Table I below in which is tabulated the deasphalting results obtained on Mid-Continent residuums using a silica-alumina gel type sorbent having a bulk density in the 4-8 mesh size range of about 0.7.

Table I

Experiment Number.....	1	2	3	4	5	6	7
Charge Viscosity, S. U. V.....	116.9	81.8	340	116.9	81.8	81.8	81.8
Charge, Ramsbottom Carbon.....		2.3	5.1		2.3	2.3	2.3
Mesh Size of Sorbent (Tyler).....	4-8	4-8	4-8	30-60	30-60	60-80	30-60
Sorption Zone Contact Time.....	24 hrs.	72 hrs.	4 hrs.	24 hrs.	2 min.	2 min.	2 hrs.
Sorption Zone Temperature, °F.....	150	75	275	150	150	150	150
Weight Ratio of Sorbent To Liquid Charge.....	1	1	2.2	1	1	1	1
Properties of Oily Constituents Retained By Sorbent after Washing:							
S. U. V. @ 210° F. Sec.....	69.7	49.7	151	129.2	75.2	81.7	115.4
Ramsbottom Carbon, percent.....			2.4		1.8	2.3	3.1
Properties of Materials Washed from Sorbent Surface:							
S. U. V. @ 210° F. Sec.....	164	139.2	650	100.1	85.9	80.5	76.0
Ramsbottom Carbon, percent.....		3.5	6.7		2.4	2.2	2.0

diameter not exceeding about 125 Angstrom units and a particle size usually not smaller than about 60 mesh and preferably larger than 30 mesh have the ability to sorb the oily constituents of a liquid hydrocarbon fraction while leaving substantially unsorbed the asphalt constituents. Natural and treated clays and bauxites such as are employed in oil filtering and decolorizing process do not appear to have this property. The macropore volume of the contact material employed in the present invention should be relatively low so that the pore volume is mostly that of micropores. In general, the volume of macropores, that is, structure corresponding to that of an inorganic oxide gel having a substantially uniform porosity those pores having radii larger than 100 Angstrom

It will be apparent from the above Table I that when the gel type sorbent particles were greater than 30 mesh size that even at relatively high temperatures and long contact periods the oily constituents of low viscosity and carbon residue were sorbed in the pores of the sorbent while the asphaltic constituents could be washed away with a suitable washing solvent, in this case benzol. On the other hand, in the case of sorbent particles ranging from 30-60 mesh size, when the contact period was 24 hours (Experiment 4) or even 2 hours (Experiment 7), the sorbent acted similar to a normal filtering clay and preferentially adsorbed the asphaltic constituents. But when the contact time was reduced to two minutes (Experiment 5), the 30-60 mesh sorbent ex-

hibited a preference for the oily constituents over the asphaltic constituents. When the particle size was reduced below 60 mesh, the sorbent preferentially adsorbed the asphaltic constituents even at very low contact periods (Experiment 6).

The effect of contact time and temperature is shown in Table II below in which the deasphalting results on an East Texas residuum having an original Saybolt Universal viscosity of 512 seconds at 210° F. and a Ramsbottom carbon residue of 11.1. In this experiment a silica-alumina gel type sorbent of 4-8 mesh size and 0.48 bulk density was employed.

Table II

Experiment Number.....	1	2	3
Sorption Zone Contact Time, Hours.....	4	4	2
Sorption Zone Contact Temperature, °F.....	275	300	300
Sorbent to Oil Weight Ratio.....	1.6	1.4	1.5
Ramsbottom Carbon Residue, Percent of Sorbed Oily Constituents.....	1.9	2.6	2.0

In general it may be said that the particle size of the sorbent material particularly in the case of inorganic oxide gel type sorbents should be less than about 60 mesh Tyler and preferably within the range about 0.022 to 1.0 inch average diameter. The best results may be obtained by limiting the sorbents within the range 0.03 to 0.20 inch average diameter and of reasonably uniform size. It is pointed out, however, that by proper control of the variables discussed hereinabove and also of the average pore diameter of the sorbent, operation according to the method of this invention may be obtained on sorbent particles outside the size ranges given although the results will be less satisfactory. It is contemplated that in its broader aspects this invention covers these latter operations as well as the operations within the specified preferred limits.

The porosity of the gel particles employed in the process of this invention is of fundamental importance. The degree of porosity is generally reflected in the bulk density of the gel composite used; the lower the bulk density, the greater being the degree of porosity. For the purposes of the present process, porous sorbent particles having bulk densities between about 0.4 and 1.1 gram per cubic centimeter are preferred. The bulk densities indicated correspond to an average pore diameter of between about 20 and about 125 Angstrom units. Preferably, the sorbent used will have a bulk density between about 0.6 and about 0.8 gram per cubic centimeter. Gel particles having a bulk density greater than about 0.8 have been found to have excellent selectivity but poor sorbing capacity, while particles with a bulk density less than about 0.6 have relatively poor selectivity. However, since the selectivity of the deasphalting process improves with a decrease in temperature, particles with a bulk density less than 0.6 would be satisfactory for deasphalting stocks which can be processed at low temperatures.

The degree of porosity of a synthetic inorganic oxide gel will, in general, depend on the conditions under which it is prepared and allowed to set to gelation. A particularly convenient method of preparing gel particles used in the process of this invention is described in U. S. 2,384,946, issued September 18, 1945, to Milton M. Marisic. It is there disclosed that spheroidal particles of inorganic oxide gel may be prepared by mixing an acidic stream with a stream of sodium silicate and allowing the resulting sol to be ejected

from a nozzle into an oil column, where the gel sets in the form of bead-like spheroids. The resulting gel spheres, after washing, drying and tempering, were of a size varying between about 4 and about 20 mesh. The gel beads so produced had a bulk density of between about 0.4 and about 1.1 and an average pore diameter of between about 20 and about 125 Angstrom units. They proved to be excellent selective adsorbents for use in the process of this invention.

Likewise, irregularly shaped porous absorbent fragments or particles having the structure of inorganic oxide gels may be used. However, in general, spheroidal particles are to be preferred, since attrition losses are then at a minimum and contamination with gel fines of the asphalt-bearing stock is substantially eliminated.

In general, siliceous gel particles will be used in the process of this invention, such as silica gel, silica-alumina gel, silica-zirconia gel, silica-thoria gel and the like. Porous sorptive silica glasses having a structure approaching that of a siliceous gel likewise are contemplated for use in the process described herein, it being necessary, however, that the porous glasses employed have an average pore diameter less than about 125 Angstrom units, and a macropore volume of less than about 30 percent of the total pore volume. The size of the porous glass particles must also be carefully controlled so as to obtain preferential sorption of the oily constituents. Usually particles of less than 60 mesh size are undesirable. It is also contemplated that within the scope of this invention other porous materials not of the inorganic oxide gel composition which have structures approaching that of a siliceous gel and are within the above specified pore size and particle size limits may be employed within the scope of this invention.

Typical of the porous glasses used are those described in U. S. 2,106,744, issued February 1, 1938, to Hood et al. There it is disclosed that a silica-alkali-boric oxide glass of suitable composition is prepared by a fusion process. Heat treatment of this glass results in separation of the glass into two phases; one phase is rich in alkali-boric oxide and is soluble in acids, while the other phase, which is insoluble in acid, consists of silica with a small amount of boric oxide. Extraction of this heat treated glass with acid results in a porous silica glass which can be employed as a porous absorbent separating medium in accordance with the present invention.

The invention may be most readily understood by reference to the drawings attached hereto of which:

Figure 1 is a schematic arrangement of the system of this invention in which some of the apparatus is shown partially in section;

Figure 2 is a similar view showing a modified arrangement of the converter which may be employed in the total combination shown in Figure 1.

All of these drawings are highly diagrammatic in form.

Turning now to Figure 1, for a study of the process of this invention, vessel 20 is a deasphalting chamber which may be of rectangular or any other desired cross-sectional shape. A partition 24 across the upper section of chamber 20 defines a solid inlet surge chamber 25 in its upper end. Tubes 26 depend from partition 24 for flow of contact material from chamber 25 onto the surface of the substantially compact contact material column maintained in the sorption section

28 of the deasphalting vessel. Particle form contact material having a catalytic activity for the desired conversion and being suitable for sorbing the oily constituents of a liquid feed while leaving substantially unsorbed the asphalt constituents thereof is cooled to a suitable temperature in hopper 29 positioned above vessel 20 and then passed via conduit 21 into vessel 20 to keep replenished the column of such material in section 28 of vessel 20. A hydrocarbon feed stock which contains both asphaltic and oily constituents, for example, a heavy petroleum residuum fraction or a tar separator bottoms fraction, is introduced into chamber 20 from manifold 10 via headers 11, closed on their ends, which extend into space 30 and nozzles 12 which are spaced along headers 11. The liquid charge distributes itself over the surface 27 of the contact material column and percolates downwardly within the column, whereby the oily constituents become sorbed in the pores of the contact material and the asphalt constituents remain substantially unsorbed. The contact material bearing sorbed oily constituents and the unsorbed liquid are withdrawn together from the bottom of vessel 20 through duct 22 at a suitable rate controlled by the valve 31.

The mixed liquid and solid material are directed by duct 22 onto an endless foraminous moving belt 14 supported over horizontally spaced pulleys 15 and 16, the latter of which is rotated by means of drive motor 17. The drain duct 22 and valve 31 therein may extend horizontally substantially the width of belt 14 so as to uniformly distribute solid material and liquid across the belt. Suitable guards (not shown) may be provided within chamber 35 along the opposite sides of the belt 14 to prevent solid particles from falling off the sides. A drain pan 18 is supported on its opposite sides from the wall of chamber 35 between the pulleys 15 and 16 and below the belt 14 so as to receive liquid which drains therethrough. The drained liquid containing the asphalt constituents is withdrawn from pan 18 via conduit 19 to the asphalt receiver 32. Entrained solid fines may be removed from the bottom of receiver 32 by means of outlet 33 and asphalt may be withdrawn via conduit 34 to pump 36. The asphalt containing liquid then may be entirely pumped from the system via conduits 37 and 38 or in part recycled via conduits 37 and 39 to inlet manifold 10 feeding the deasphalting chamber. In some operations such recycling is desirable in order to reduce the amount of oily material in the finally discarded asphalt constituents to a minimum.

The contact material is carried along on belt 14 in the direction of the flow arrows and the contact material from which most of the unsorbed liquid has been separated by draining is discharged from the belt 14 onto the washing chamber 40. The chamber 40 communicates on its lower end with the boot section of a bucket elevator 43. In elevator 43 buckets 44 having perforated bottoms are moved upwardly and downwardly on endless chain 45 so as to transfer the washed contact material from the elevator boot section upwardly to duct 350 feeding supply hopper 46 which in turn feeds the hydrocarbon converter 47. The bottoms of the elevator buckets 44 are perforated, the perforations being of such size as to retain the contact material particles while permitting liquid to pass therethrough. The elevator casing is inclined and the buckets are so shaped that liquid which drains from any given upwardly moving bucket does not fall into

the bucket moving upwardly therebelow, but is delivered back to the elevator boot section. A suitable washing solvent such as a naphtha, kerosene, benzol or light gas oil fraction may be introduced from an outside source through conduit 48 through which it passes into the elevator boot section. The solvent passes from the elevator boot section into the lower section of chamber 40 via passage 49 and then passes upwardly through the washing chamber to be withdrawn from the upper portion thereof through conduit 50 to a washing receiver 51. The solvent is pumped from receiver 51 by pump 151 through pipe 49 to a suitable fractionator (not shown) wherein it may be separated from the asphalt material. Baffles 52 provide a zig-zag passage in chamber 40 through which the contact material passes as it descends through the bath of upwardly moving washing solvent. The solid particles are in this manner subjected to a quick wash under conditions so controlled as to accomplish the removal of asphalt containing liquid adhering to the outer surfaces of the contact material particles without substantial separation of the sorbed oily constituents from the contact material. A relatively small amount of washing solvent may also be sorbed by the contact material during the washing operation. The washed contact material may thus contain a substantial amount of sorbed oily constituents from the original feed, a relatively small amount of washing solvent (and in some cases practically no washing solvent) and in some instances small amounts of asphalt constituents from the feed. It should be understood that while the gel type contact material particles of the type described have the unusual characteristic of sorbing oily constituents rather than asphalt constituents from high boiling feeds, nevertheless, in the case of some feed fractions the gel type catalyst will also sorb relatively small amounts of asphalt materials. It has been found that this relatively small amount of sorbed asphaltic materials will not increase the coke deposits on the catalyst to prohibitive levels. It should be understood that in claiming this invention in the expressions "while leaving the asphalt constituents substantially unsorbed"; or contact material suitable for sorbing "substantially only the oily constituents of the liquid feed" and in like expressions the word substantially is intended to allow for these relatively small amounts of asphalt constituents which may in some operations be sorbed along with the much larger amount of oily constituents in the contact material pores.

The washed contact material bearing sorbed oily constituents may be passed from the converter supply hopper 46 into the upper end of converter 47 as a substantially compact, elongated gravity feed leg flowing downwardly in conduit 55. Within the upper section of converter 47 a horizontal partition 56 is positioned so as to define a seal chamber 57 in the upper end of the converter. It is into this seal chamber 57 that the contact material feed is delivered.

A suitable inert seal gas such as steam or flue gas may be introduced into seal chamber 57 at a rate sufficient to maintain a gaseous pressure therein above that in the conversion section of vessel 47. Conduit 130, diaphragm valve 131 and differential pressure control instrument 132 are provided for this purpose. A plurality of uniformly spaced vertical conduits 58 serve as a passage for solid flow from seal chamber 57 onto the column 59 of contact material maintained

in a lower section of the convertor. A hot gas inlet connects into the space 60 provided around the conduits 58. A line heater 160 is provided on conduit 61. This heater may be of conventional construction adapted for heating air or for producing hot flue gas and is provided with a fuel inlet 62 and an inlet 63 for oxygen or air. A plurality of vertically spaced rows of horizontal, perforated fuel gas distributing tubes are provided within the convertor 47. Two such rows 64 and 65 connecting on their open ends to headers 66 and 67 respectively are shown, but it will be understood that more than two rows may be provided. The pipes 64 and 65 are closed on their ends which terminate within the convertor. The headers 66 and 67 connect into a fuel gas inlet manifold 150 and valves 151 and 152 are provided on headers 66 and 67 respectively to permit independent control of the gas flow to each row of distributing tubes. A similar row of oxygen distributing tubes is provided a spaced distance above each row of fuel gas tubes. Two rows of oxygen tubes 153 and 154 connecting into headers 155 and 156 respectively are shown. The headers 155 and 156 carry flow control valves 157 and 158 respectively and connect into an oxygen gas inlet manifold 159. The arrangement is such that the relatively cool contact material bearing sorbed oily constituents is heated to a temperature at which fuel gas and oil combustion will occur by the passage of hot gas introduced via conduit 61 downwardly through the column 59. The gas entering at 61 is heated to a suitable level in heater 160 and may contain controlled amounts of oxygen or substantially no oxygen at all. The gas may enter at temperatures of the order of 800° F. and upwards and may heat the contact material supplied into the column 59 at about 400° F., for example to a temperature of the order of 800° F.-900° F., for example, by the time the contact material reaches the first row of oxygen gas distributing tubes 153. Oxygen, air or mixtures of oxygen and inert gases are introduced into the column from tubes 153 and 154 at rates controlled to accomplish only sufficient combustion of the hydrocarbon compounds on the contact material as is required to supply the heat required for the desired conversion of the sorbed oily constituents and to maintain the contact material within the range of temperatures required to effect said conversion. For example, in the case of a catalytic cracking conversion the catalyst may preferably be controlled at some level within the range about 800° F.-950° F. On the other hand if the reaction is dehydrogenation, the catalyst may be controlled at some level within the range 900° F.-1200° F.

If desired, instead of relying on combustion of part of the sorbed oily constituents to supply the heat for the hydrocarbon conversion, controlled amounts of gaseous hydrocarbon fuels may be introduced into the catalyst column through tubes 64 and 65. This latter operation is particularly desirable in those instances wherein the desired conversion temperature range is too low for combustion of the sorbed oily constituents at practical rates. In either operation the amount of oxygen added is so small that only a partial oxidation of a small portion of the sorbed oily constituents occurs and the remainder of the oily material is converted into valuable hydrocarbon products such as gasoline, naphtha and gas oils.

The mixed gaseous products resulting from

the catalytic conversion of the sorbed oily constituents are withdrawn from the lower section of vessel 47 by means of spaced rows of inverted collecting troughs 80 and 80' provided with outlet pipes 81 and 81'. The pipes 81 and 81' connect into manifolds 82 and 82' respectively from which the gaseous products are withdrawn through conduits 83 and 83' respectively which merge into a single outlet conduit 84. Valves 85 and 86 are provided on conduits 83 and 83' respectively to permit control of the amount of the rate of gas withdrawal at each level of collectors. The gaseous products are then passed to a suitable fractionator and separation system which may be of the construction conventional to the petroleum industry. It is pointed out that the term "gaseous" as used herein in describing and in claiming this invention is intended in the sense of covering materials which are in the gaseous phase under the particular operating conditions involved regardless of the normal phase of those materials under atmospheric conditions. For example, gaseous conversion products leaving the convertor through conduit 84 at a temperature of the order of 800° F. to 950° F. and say 10 pounds gauge pressure may exist substantially entirely in the gaseous phase under these conditions although gasoline, gas oil and heavy fuel oil constituents may be present which are ordinarily liquids under atmospheric conditions. The gaseous products may also contain small amounts of oxidized hydrocarbons such as aldehydes, ketones, organic acids and alcohols which may be conveniently removed from the hydrocarbon products by solvent extraction. Suitable solvents for this purpose are sulfur dioxide, methyl and ethyl alcohols, acetone and polar liquids incompletely miscible with gasoline. Returning again to the conversion vessel 47, there is provided in the lower section of vessel 47 two horizontal, vertically spaced partitions 88 and 89. A plurality of uniformly distributed tubes 90 depend from partition 88 and a smaller plurality of orifices 91 are provided in partition 89. The orifices 91 are horizontally offset with respect to tubes 90 so as to proportionately receive streams of contact material therefrom and to cause them to merge into a smaller plurality of streams which in turn merge into a single outlet stream in outlet conduit 93. The arrangement is such as to provide for uniform withdrawal of contact material from all portions of the horizontal cross sectional area of vessel 47 through the outlet 93. This arrangement is fully described and claimed in United States application Serial Number 473,861, filed January 28, 1943, now Patent No. 2,412,136 in which the present applicant was one of the applicants.

A suitable purge gas such as steam or flue gas may be introduced into the lower section of vessel 47 through conduit 135 in order to purge the outflowing used contact material substantially free of the lower boiling conversion products.

It will be noted that in the operation described thus far the inorganic gel type contact material particles serve the dual function of serving as an unusual sorbent permitting separation of asphaltic constituents from the oily constituents of the original feed fraction and also as a catalyst to promote the conversion of the oily constituents in vessel 47 once a suitable conversion temperature has been reached.

The used contact material which is withdrawn from vessel 47, substantially separately of the gaseous conversion products, through conduit 93

11

and throttle valve 94 thereon has lost a substantial part of its catalytic effectiveness due to deposition of a carbonaceous contaminant thereon. The used contact material is, therefore, transferred by conveyor 95 to chute 96 feeding the regenerator 97. A surge chamber 98 is provided in the upper end of regenerator 97 to receive the used contact material. The regenerator shown in Figure 1 is of the multi-stage variety which is described and claimed in application Serial Number 447,432, filed in the United States Patent Office June 17, 1942, now Patent No. 2,417,399 and application Serial Number 447,433, filed in the United States Patent Office June 17, 1942, now Patent No. 2,436,780 in which applications the present applicant is one of the applicants. In general the regenerator 97 is divided into a vertical series of alternating burning and cooling stages. Separate gas inlets 99, 100, 101 and 102 and separate gas outlets 104-107, inclusive, spaced vertically from the inlets, are provided for the burning stages. The gas inlets are supplied by a combustion supporting gas such as oxygen, air or mixtures of air and flue gas, from inlet manifold 108. Flue gas passes from the burning stages through outlets 104-107 and is manifolded into outlet flue 109. If desired, part of the hot flue gas from flue 109 may be introduced into the convertor 47 through conduit 61 in place of hot gases from heater 160. Heat transfer tubes or coils (not shown) may be suitably spaced within the cooling stages. Pipes 110 are inlets to these tubes and pipes 111 are outlets therefrom. The inlet pipes 110 connect into an inlet manifold 112 and the outlet pipes 111 connect into an outlet manifold 113. The excess heat released by burning the carbonaceous contaminant from the contact material may be carried by a suitable heat exchange fluid passing from outlet manifold 113 through conduit 114 to steam drum 115 wherein water is evaporated to provide high pressure steam in drum 115. The fluid may then pass from drum 115 to pump 117 by which it is forced through conduit 118 into the inlet manifold 112 which supplies the heat transfer tubes in the regenerator cooling stages through pipes 110. The heat exchange fluid may take any of a number of forms such as a suitable gas under pressure or fused metallic oxides or mixtures of certain fused inorganic salts.

Hot regenerated contact material is withdrawn from the lower end of regenerator 97 through outlet 119 at the desired rate as controlled by throttle valve 120. The hot regenerated contact material is then transferred by conveyor 121 to hopper 29 from which it passes into the deasphalting chamber 20 as the contact material supply thereto. The regenerated contact material in hopper 29 is cooled to a temperature suitable for its introduction into deasphalting chamber 20 by means of a suitable heat exchange fluid introduced at 68 and removed at 69. If desired, heat transfer tubes may be provided in both hoppers 29 and 46; and the heat exchange fluid withdrawn from the heat transfer tubes in hopper 29 via conduit 69 may be introduced into the tubes in hopper 46 through conduit 70. The heat recovered from the final cooling of the regenerated contact material may thereby be utilized for partially heating the cooler, oily constituent bearing contact material in hopper 46. The heat exchange fluid, relieved of its heat in hopper 46 may be withdrawn from the tubes therein through conduit 71 and reintroduced into the tubes in hopper 29 through conduit 68. A pump 72 may be provided to cyclically circulate the heat exchange fluid and an ex-

12

changer 73 may be provided to permit any heat adjustments that may be required by the desired contact material outlet temperature from hoppers 29 and 46. Heat may either be added or withdrawn by means of exchanger 73 as the particular operation involved requires.

While the system described hereinabove is one of the preferred forms of this invention, it should be understood that the various elements making up the particular combined system described are shown in highly diagrammatic form in Figure 1 and that the invention is not intended to be limited to the particular detailed construction of the various elements as shown. For example, while it is preferred to percolate the liquid charge downwardly through a column of the gel particles in the deasphalting chamber, nevertheless it is contemplated that within the scope of this invention the contacting of the gel particles and the liquid charge may be accomplished in a number of other ways and any method which permits the desired contacting is considered to be within the scope of this invention. For example, the liquid charge and the gel particles might be merely charged to a batch type mixer provided with suitable mechanical mixing devices and after suitable mixing has been accomplished, the material may then be discharged from the mixer to a suitable liquid solid separator. Likewise other methods and apparatus than that described hereinabove may be employed to effect separation of unsorbed liquid material from the contact material bearing sorbed oily constituents. For example, a rotary type filter provided with suitable means for accomplishing both filtering off of unsorbed liquid and washing of the contact material may be employed. In some operations the washing step may be eliminated entirely and the combination of draining and purging of the contact material with a suitable purging gas may be relied upon to separate the contact material from unsorbed asphalt containing liquid. Moreover, while in the system described hereinabove the washed contact material was partially heated and then charged through a gravity feed leg to the convertor, it is contemplated that the preliminary partial heating step may be eliminated and all of the heating accomplished within the convertor. Also suitable forced feed devices may be substituted for the gravity feed leg in less preferred forms of the invention as means of introducing the contact material bearing sorbed oily constituents into the convertor. It is also contemplated that the convertor and regenerator construction may be materially different from that shown in Figure 1. Other suitable means for distributing the oxygen containing gas into the column within the convertor 47 may be substituted for that shown as will be readily apparent to those skilled in the art. Other suitable means for removal of gaseous products from the conversion zone may be employed where desired and in some operations the contact material and conversion products may be withdrawn together and then separated. The regenerator may be of the single stage type and also of the other types which will be described hereinafter, if desired.

Since the inorganic oxide gel type contact material involved is preferably of 30 mesh size and larger it is more practical and desirable in order to prevent undue attrition of the contact material to handle the contact material as a substantially compact moving bed or column in the convertor and regenerator and to convey it between

vessels by continuous bucket elevators. However,

with the broader scope of this invention it is contemplated that the contact material may move in suspension in a suitable gaseous stream or as a fluidized mass within the conversion and regeneration vessels; and that means other than bucket elevators may be employed for transferring the contact material from one zone to another. It is further contemplated that within its broader scope the method of this invention may involve a substantially "in situ process" wherein the contact material remains permanently in one or more vessels. For example, the deasphalting, draining, washing, heating conversion and catalyst regeneration and cooling steps may be conducted in proper cycle in a single chamber in which the contact material particles remain as a fixed bed. A batch type operation wherein the contact material is moved periodically, batchwise from zone to zone is also contemplated.

It will be understood that the desirable conditions of operation during the deasphalting, washing, conversion and catalyst regeneration and cooling steps will vary depending upon the particular liquid charge stock involved and the conversion reaction involved and the particular conversion products desired. Certain general conditions of operation must, however, be observed. As regards the deasphalting operations the temperature at which the sorption of oily constituents by the particle-form gel type contact material is conducted should be high enough to give the oil sufficient fluidity to permit rapid sorption of the oily constituents but low enough to permit the contact material to function selectively. The maximum temperature maintained in the sorption zone is dependent on the viscosity of the stock being treated. The sorption of oily constituents becomes less selective as the viscosity decreases. The desirable sorption temperature has been found to vary from below room temperature to about 500° F. depending on the liquid fraction treated. The temperature of the hydrocarbon liquid charged into the sorption zone and the contact material supplied therinto should be both adjusted to provide the desired sorption temperature. The contact material should not be permitted to contact the asphalt containing liquid feed at temperature at which substantial thermal coking of the liquid fraction would take place. This means that in general the contact material should be cooled in hopper 29 of Figure 1 for example, to a temperature which is at least below about 750° F. The pressure in the sorption zone may conveniently be within the order of atmospheric to 50 pounds per square inch. The residence time of the contact material within section 28 of chamber 20, i. e. the sorption zone, may vary from about 1-10 hours depending upon the liquid fraction involved, the temperature and the ratio of the contact material to the liquid charge. In many operations it is desirable to control the residence time of the contact material in chamber 20 by means of valve 31 such as will permit substantial saturation of the contact material with sorbed oily constituents.

The ratio of contact material to liquid charge to the deasphalting chamber may vary from about 0.5 to 20 parts by weight of contact material per part of liquid asphalt bearing charge and preferably from about 2 to 6 parts of contact material per part of liquid charge.

The amount of solvent employed in the washing operation may vary depending upon the characteristics of the solvent and of the unsorbed liquid involved. In general the contact material

washing should be a relatively "quick wash" so controlled as to prevent removal by the solvent of substantial amounts of sorbed oily constituents from the contact material. The amount of solvent employed may be of the order of 0.25 to 2.0 volumes of solvent per volume of contact material. In some operations the purging step following the washing step may be omitted but when this step is employed the purging gas employed should be a gas which is not apt to cause oxidation of the oily constituents during the conversion, unless of course, the conversion process involved is a partial oxidation process. Steam, nitrogen, flue gas and low molecular weight hydrocarbon gases are suitable purging gases for most operations.

As an example of the operation during the deasphalting and washing steps of this process the treatment of an East Texas crude bottoms fraction having an A. P. I. gravity of 15.0 at 60° F., a Saybolt Universal viscosity of 512 seconds at 210° F., a pour point above 115° F., and a Conradson carbon residue of 11.1 percent may be considered. The vacuum assay distillation of this feed fraction was as follows:

I. B. P. _____	° F.
10% _____	880
30% _____	964
40% _____	1026
47% _____	1054
	1082

This feed fraction was contacted in a suitable confined chamber with a silica-alumina, spherical gel catalyst prepared by the method described in United States Patent 2,384,946 issued September 18, 1945, to Milton Marisic. The catalyst unpacked density was about 44 pounds per cubic foot and consisted of particles falling within the range 4 to 16 mesh by Tyler standard screen analysis. The catalyst had been regenerated until the residual carbon thereon was below 0.5% by weight. During the operation the temperature was maintained at about 275° F. and the pressure was substantially atmospheric. The ratio of liquid to catalyst charge to the sorption zone was about 3.2 parts by weight of catalyst per part by weight of liquid charge. The residence time within the sorption zone was about 240 minutes. The unsorbed liquid was recycled until substantially all of the oily constituents had been removed therefrom. Finally a tar fraction amounting to about 30 percent by weight of the liquid charge was separated from the catalyst bearing sorbed oily constituents and the catalyst was washed with about half of its weight of Stoddard solvent, the residence time of the catalyst in the washing operation being limited to about 3 minutes. The catalyst after washing contained about 22 percent of its original weight of sorbed oily constituents which represented about 70 percent by weight of the original liquid charge.

When the contact material bearing sorbed oily constituents is partially heated before introduction to the conversion zone as shown in Figure 1, it should be heated only to a temperature which is substantially below the desired conversion temperature. Usually a temperature of the order of 750° F. is the maximum temperature to which the contact material should be heated in hopper 46 of Figure 1. As has been pointed out, the contact material introduced to chamber 20 should be below about 750° F. so that regenerated contact material in hopper 29 of Figure 1 should be cooled to a level at least below about 750° F.

The operating conditions within the convertor

47 will vary depending upon the activity of the catalyst employed, the particular petroleum charge involved, the reaction involved and the products desired. In general it has been found desirable to maintain the pressures within a range varying from sub-atmospheric to about 200 pounds per square inch. Pressures of the order of 5 to 50 pounds per square inch gauge are preferred. The temperature for the conversion for cracking operations may vary from about 750° F. to 1100° F., temperatures of the order of 850°-1000° F. being preferred where gasoline is the desired product. Where non-condensable gases are the principal desired product and for dehydrogenation reactions somewhat higher temperatures may be employed. The ratio of contact material to hydrocarbon throughput may vary from about 1.0 to 40 parts by weight of contact material per part of hydrocarbon charge. The amount of oxygen introduced into the conversion zone should be controlled with reference to the catalyst temperature so as to control the catalyst temperature at the proper level for effecting the conversion of the oily constituents.

In the contact material regenerator, pressures of the order of atmospheric to about 100 pounds per square inch may be employed, pressures around atmospheric being preferred. The contact material temperature should be controlled below a heat damaging level by removal of heat therefrom during the course of the contaminant burning. The heat damaging level is that level at which and above which the contact material suffers permanent loss in catalytic effectiveness for the conversion involved or loss in sorptive efficiency. The heat damaging temperature may vary from temperatures above about 1150° F. to temperatures above about 1450° F. depending upon the particular gel type catalyst involved.

While in the system shown in Figure 1 the oxidizing gas passes through the convertor concurrently with the catalyst flow, it is also contemplated that the gas may flow countercurrently with the catalyst flow. Such an arrangement is shown in Figure 2 in which only the convertor portion of the system is shown. It will be understood that the convertor system shown in Figure 2 may be substituted in the complete arrangement shown in Figure 1 for the convertor system shown therein. Corresponding elements shown in Figures 1 and 2 bear like numerals and need not be again discussed in detail. In Figure 2 three rows of air or oxygen distributing tubes 170, 171 and 172 are provided within the convertor 47. These tubes are supplied with oxygen from conduit 174 and manifold 175 through headers 176, 177 and 178 respectively. A row of hot gas distributing troughs 179 supplied through pipe 180 is provided in the lower section of the convertor. The gaseous reactant outlet is located in the upper section of convertor 47 at 181.

In operation contact material bearing sorbed oily constituents enters the convertor seal zone 57 through feed leg 55 and passes from seal zone 57 through pipes 58 onto the column 59 in the conversion zone. Air or oxygen containing gas is introduced into the column through distributors 170-172 and through troughs 179 when fed by pipe 182. The air burns some of the oily constituents and carbonaceous material on the contact material thereby releasing heat so as to cause conversion and vaporization of the oily constituents on the contact material. The vaporized hydrocarbon reaction products as well as the combustion products pass upwardly through the

column 59 and gradually raise its temperature. Thus there is a gradual increase in contact material temperature as it moves downwardly through the upper portion of the convertor until it reaches the desired hydrocarbon conversion temperature. At lower levels the column temperature may be maintained substantially constant within a controlled range by proper control of the rate of oxygen containing gas introduction at the several levels along the convertor. In this modification, the hot gas heater 160 need be employed only in initiating the operation, after which the valve 183 may be closed and the oxygen or air valve 182 opened. The spent contact material is withdrawn from the lower section of convertor 47 through conduit 93 and passed to a suitable regenerator such as the regenerator 97 shown in Figure 1. It then passes through the same cycle as does the contact material in the system of Figure 1. The mixed gaseous products pass via conduit 181 through condenser 185 and then through conduit 186 to separator 187 wherein the non condensed gas is separated from the condensed products. The non condensed products are withdrawn through 188 to a suitable fractionator system (not shown) and the liquid products pass via conduit 190 to pump 191 by which they may be pumped to storage or to a suitable product recovery system through conduits 192 and 193. On the other hand in view of the fact that some of the conversion products are removed from the contact material in the upper section of convertor 47 and have been insufficiently contacted with catalyst to effect complete conversion, it is often desirable to pass the liquid conversion products from convertor 47 through a secondary convertor. In this operation the liquid hydrocarbons are pumped through heater 194 and then pass via pipe 195 into convertor 196. In some operations it is desirable to pass the total gaseous products from convertor 47 through the secondary convertor in which case the by-pass conduit 210 is employed. The hydrocarbons in the gaseous phase may pass up through a moving column of catalyst in convertor 196 whereby final conversion is effected. The final conversion products are withdrawn from the upper section of the convertor at 197. It will be understood that the secondary convertor may be any of a number of conventional types involving either moving or stationary catalyst. The convertor shown is of the moving bed type similar to convertor 47 being supplied from hopper 198 through feed leg 199 with freshly regenerated hot catalyst. The spent catalyst from convertor 196 is withdrawn via conduit 200 and passed to a suitable regenerator of conventional type. The catalyst and conversion conditions in convertor 196 may be the same as in convertor 47 or may differ somewhat depending upon the particular products desired.

By the method of this invention a high octane gasoline product may be prepared as well as oxygen containing carbon hydrogen compounds as by-products. These valuable products are prepared from crude residuums, tar separator bottoms and other asphalt containing hydrocarbon fractions which have heretofore been considered as unfit as catalytic conversion charging stocks. By the initial deasphalting step the amount of coke formed during the conversion may be kept within practical commercial limits, yet the expensive solvent extraction processes by which deasphalting is usually accomplished are avoided.

The heat exchange between hoppers 29 and 46 of Figure 1 permits the change in the level of catalyst temperature between the deasphalting and conversion steps without excessive external heating or cooling requirements. By burning a small portion of the sorbed oily constituents to supply the heat required for the conversion and for final heating of the catalyst in the convertor and by feeding the oil charge into the convertor sorbed on the catalyst, the oil charge pumps and oil preheaters conventional in the art have been entirely eliminated.

It should be understood that the details of apparatus construction and arrangement, of operating conditions, and of applications of the process of this invention given hereinabove are intended merely as illustrative and it is not intended that the scope of this invention should be limited thereto or limited otherwise except as it may be limited in the following claims.

I claim:

1. A process for conversion of oily constituents present in liquid fractions containing oily and asphalt constituents at elevated temperatures which comprises: sorbing said oily constituents from the liquid hydrocarbon fraction into the pores of a porous contact material the particles of which are greater than about 60 mesh size and in which less than 30 percent of the total pore volume is occupied by pores having radii greater than about 100 Angstrom units while leaving substantially unsorbed the asphalt constituents and heating the contact material bearing sorbed oily constituents in substantial absence of the unsorbed asphalt constituents by passing an oxidizing gas into contact with said contact material to oxidize a portion of the oily constituents and thereby release sufficient heat to heat said contact material to a temperature suitable for the conversion of remaining oily constituents to hydrocarbon products.

2. A process for conversion of oily constituents present in liquid fractions containing oily and asphalt constituents at elevated temperatures which comprises: contacting a liquid fraction containing oily and asphalt constituents with a particle form porous contact material in which the pores are mostly micropores, the volume of pores having radii greater than about 100 Angstrom units being less than about 30 percent of the total pore volume, controlling the relative relationships of contact time and temperature and of particle size to effect sorption of the oily constituents of said fraction into the pores of the contact material particles, effecting a substantial separation of the unsorbed liquid from the contact material which bears the sorbed oily constituents, passing oxygen into contact with said contact material under conditions suitable for oxidation of some of said oily constituents and controlling the rate of oxygen flow to effect by the oxidation reaction heat release the heating of said contact material to a temperature suitable for the conversion of said oily constituents.

3. A process for conversion of the high boiling oily constituents in asphalt bearing hydrocarbon liquid feeds to lower boiling products which comprises: contacting said liquid feed for a suitable time and at a suitable temperature with a porous particle-form inorganic oxide gel-type contact material in which most of the pores are micropores and the volume of pores having radii larger than about 100 Angstrom units is less than about 30 percent of the total pore volume and in which the particles are greater than about 30 mesh size

to effect the sorption of the oily constituents of said feed in the pores of said contact material while leaving the asphalt constituents substantially unsorbed; effecting a substantial separation of the unsorbed liquid from the contact material which bears the sorbed oily constituents; introducing an oxygen containing gas into contact with said contact material under conditions suitable for partial oxidation of said oily constituents with a resultant liberation of heat, and limiting the rate of oxygen containing gas introduction substantially to that required to supply by said heat liberation the heat required to heat said contact material to and maintain it at a temperature suitable for the conversion of said oily constituents to lower boiling products.

4. A process for conversion of the high boiling oily constituents in asphalt bearing hydrocarbon liquid feeds to lower boiling products which comprises: contacting said liquid feed for a suitable time and at a suitable temperature with a porous particle-form inorganic oxide gel-type contact material in which most of the pores are micropores and the volume of pores having radii greater than about 100 Angstrom units is less than about 30 percent of the total pore volume and in which the particles are greater than about 60 mesh size to effect the sorption of the oily constituents of said feed in the pores of said contact material while leaving the asphalt constituents substantially unsorbed; effecting a substantial separation of the unsorbed liquid from the contact material which bears the sorbed oily constituents; heating said contact material to a temperature suitable for reacting said oily constituents with oxygen, introducing an oxygen containing gas into contact with the contact material so heated to react with a portion of said oily constituents with the resultant liberation of heat and controlling the rate of oxygen containing gas introduction to effect a further heating of said contact material to a temperature suitable for the conversion of said oily constituents to lower boiling products.

5. A process for conversion of oily constituents present in liquid fractions containing oily and asphalt constituents at elevated temperatures which comprises: contacting a liquid fraction containing oily and asphalt constituents with a porous, particle form contact material in which the pores are mostly micropores and the volume percentage of pores having radii greater than about 100 Angstrom units is less than about 30, maintaining the relationship of contact material to liquid ratio, residence time, temperature and particle size to effect sorption of the oily constituents of said fraction into the pores of the contact material particles while leaving substantially unsorbed the asphalt constituents, and effecting a heat liberating combustion reaction in the presence of said contact mass bearing sorbed oily constituents and in substantial absence of the unsorbed asphalt constituents to heat said contact material to a temperature suitable for the desired conversion of said oily constituents.

6. A process for conversion of the high boiling oily constituents in asphalt bearing hydrocarbon liquid feeds to lower boiling products which comprises: contacting said liquid feed for a suitable time and at a suitable temperature with a porous particle-form inorganic oxide gel-type contact material in which most of the pores are micropores and the volume of pores having radii larger than about 100 Angstrom units is less than

about 30 percent of the total pore volume and in which the particles are greater than about 60 mesh size to effect the sorption of the oily constituents of said feed in the pores of said contact material while leaving the asphalt constituents substantially unsorbed; effecting a substantial separation of the unsorbed liquid from the contact material which bears the sorbed oily constituents burning a gaseous fuel in direct contact with said contact material to heat it to a temperature suitable for the conversion of said oily constituents to lower boiling products.

7. A process for conversion of high boiling liquid asphalt containing hydrocarbon fractions to lower boiling products which comprises: contacting said liquid fraction for a suitable time and temperature with a porous, particle-form contact material in which the pores are mostly micropores and the volume of pores having radii larger than about 100 Angstrom units is less than about 30 percent of the total pore volume to effect sorption of the oily constituents of said liquid fraction while leaving substantially unsorbed the asphalt constituents, effecting a substantial separation of the unsorbed liquid from the contact material bearing sorbed oily constituents, passing the separated contact material through a confined zone while conducting a combustion reaction therein in the presence of said contact material to heat said contact material to a temperature suitable for effecting the conversion of said oily constituents to lower boiling products, effecting a substantial separation of said lower boiling products from the contact material and reusing the contact material after removal of said contaminant deposit for contacting liquid asphalt bearing fraction as aforesaid.

8. A process for conversion of the high boiling oily constituents in asphalt bearing hydrocarbon liquid feeds to lower boiling products which comprises: contacting said liquid feed for a suitable time and at a suitable temperature with a porous particle-form inorganic oxide gel-type contact material, in which most of the pores are micropores and the volume of pores having radii larger than about 100 Angstrom units is less than about 30 percent of the total pore volume and in which the particles are greater than about 30 mesh size, to effect the sorption of the oily constituents of said feed in the pores of said contact material while leaving the asphalt constituents substantially unsorbed; draining the unsorbed asphalt containing liquid from the contact material bearing sorbed oily constituents; subjecting the contact material to washing with a suitable solvent to remove adhering asphalt containing liquid from the outer surface of said particles; and passing the washed contact material bearing sorbed oily constituents through a confined zone while contacting it with a stream of oxygen containing gas under conditions suitable to effect partial oxidation of some of said oily constituents with resultant liberation of heat, and limiting the rate of flow of said stream of oxygen containing gas substantially to that required to effect heating of said contact material to and maintaining it at a temperature suitable for the conversion of said oily constituents to lower boiling products.

9. A process for conversion of the high boiling oily constituents in asphalt bearing hydrocarbon liquid feeds to lower boiling products which comprises: contacting said liquid feed for a suit-

able time and at a suitable temperature with a porous particle-form inorganic oxide gel-type contact material, in which most of the pores are micropores and the volume of pores having radii larger than about 100 Angstrom units is less than about 30 percent of the total pore volume and in which the particles are greater than about 30 mesh size, to effect the sorption of the oily constituents of said feed in the pores of said contact material while leaving the asphalt constituents substantially unsorbed; draining the unsorbed asphalt containing liquid from the contact material bearing sorbed oily constituents; subjecting the contact material to washing with a suitable solvent to remove adhering asphalt containing liquid from the outer surface of said particles, heating said contact material to a temperature suitable for reaction of said oily constituents with oxygen, but below that suitable for conversion of said oily constituents to lower constituents, subjecting the contact material to so heated through a confined conversion zone while contacting it with a stream of oxygen containing gas to effect oxidation of a portion of the oily constituents and further heating of the contact material, controlling the rate of oxygen containing gas flow to supply by the oxidation reaction sufficient heat to heat said contact material to a temperature suitable for the conversion of said oily constituents to lower boiling products and effecting a separation of the lower boiling products from the used contact material.

10. A process for conversion of high boiling oily constituents in asphalt bearing hydrocarbon liquid feeds to lower boiling products which comprises: contacting said liquid feed for a suitable time and at a suitable temperature with a porous, particle-form contact material in which the pores are mostly micropores and the volume of the pores having radii larger than about 100 Angstrom units is less than about 30 percent of the total pore volume and in which the particles are of greater diameter than about 60 mesh size, to effect sorption of the oily constituents of said feed in the pores of said contact material while leaving substantially unsorbed the asphalt constituents, subjecting the contact material to washing with a suitable solvent to remove adhering asphalt containing liquid from the outer surface of said particles, passing the washed contact material bearing oily constituents through a confined zone as a substantially compact column of downwardly flowing particles, introducing an oxygen containing gas into said column under conditions suitable for effecting a partial oxidation of some of the sorbed oily constituents with resultant substantial heat liberation, controlling the rate of oxygen containing gas introduction to effect by said heat liberation the heating of said contact material to a temperature suitable for the conversion of said oily constituents to lower boiling products, separating the lower boiling products from the used contact material upon which a carbonaceous contaminant has been deposited due to said conversion, passing said used contact material through a confined regeneration zone while contacting it with a combustion supporting gas to burn off said carbonaceous contaminant, controlling the temperature of said contact material below a heat damaging level in said regeneration zone, cooling the regenerated contact material to a temperature suitable for its use in contacting said asphalt bearing liquid feed and

reusing the cooled contact material for contacting asphalt bearing liquid feed as aforesaid.

11. A process for conversion of high boiling oily constituents in asphalt bearing hydrocarbon liquid feeds to lower boiling products which comprises: contacting said liquid feed for a suitable time and at a suitable temperature below about 500° F. with a porous, particle-form contact material in which the pores are mostly micropores and the volume of the pores of greater than 100 Angstrom unit radii is less than about 30 percent of the total pore volume and in which the particles are of greater diameter than about 60 mesh size, to effect sorption of the oily constituents of said feed in the pores of said contact material while leaving substantially unadsorbed the asphalt constituents, subjecting the contact material to washing with a suitable solvent to remove adhering asphalt containing liquid from the outer surface of said particles, passing the washed contact material bearing oily constituents through a confined zone as a substantially compact column of downwardly flowing particles, introducing an oxygen containing gas into said column at a plurality of spaced levels along its length under conditions suitable for effecting a partial oxidation of some of the sorbed oily constituents with resultant substantial heat liberation, controlling the rate of oxygen containing gas introduction to effect by said heat liberation the heating of said contact material to a temperature suitable for the conversion of said oily constituents to lower boiling products, withdrawing said gaseous products from the lower section of said conversion zone, withdrawing used contact material bearing carbonaceous contaminant deposits from the lower end of said conversion zone substantially separately of said gaseous products, passing said used contact material through a confined regeneration zone while maintaining its temperature above the minimum level required for rapid burning of said deposits but below a heat damaging level, passing a combustion supporting gas into contact with said contact material in said regeneration zone to burn said deposits, withdrawing the regenerated contact material from said regeneration zone, cooling said contact material to a suitable temperature below about 750° F. and reusing at least a portion of said contact material for contacting petroleum feed fraction as aforesaid.

12. A process for conversion of high boiling oily constituents in asphalt bearing hydrocarbon liquid feeds to lower boiling products which comprises: contacting said liquid feed for a suitable time and at a suitable temperature below about 500° F. with a porous, particle-form contact material in which the pores are mostly micropores and the volume of the pores having radii larger than about 100 Angstrom units is less than about 30 percent of the total pore volume and in which the particles are of greater diameter than about 60 mesh size, to effect the sorption of the oily constituents of said feed in the pores of said contact material while leaving substantially unadsorbed the asphalt constituents, subjecting the contact material to washing with a suitable solvent to remove adhering asphalt containing liquid from the outer surface of said particles, passing the washed contact material through a partial heating zone while heating it to a temperature suitable for oxidation of the sorbed oily constituents, passing the partially heated contact material through a confined conversion zone as a substantially compact column

of downwardly flowing particles, introducing an oxygen containing gas into said column at a controlled rate to effect further heating of said contact material to a temperature suitable for the conversion of said oily constituents to lower boiling gaseous products, separating the gaseous products from the used contact material upon which a carbonaceous contaminant has been deposited during said conversion, passing the used contact material through a confined regeneration zone while controlling its temperature at a level suitable for rapid burning of said contaminant but below a level which would cause substantial permanent heat damage to said contact material, passing a combustion supporting gas into contact with said contact material in said regeneration zone to burn off said contaminant, withdrawing hot regenerated contact material from said regeneration zone, cyclically passing a suitable heat exchange fluid in indirect heat transfer relationship with said hot regenerated contact material to cool the same to a temperature suitable for its introduction into said deasphalting zone and in indirect heat transfer relationship with the washed contact material in said partial heating zone to partially heat said washed contact material as aforesaid.

13. A process for the conversion of the high boiling oily constituents present in high boiling petroleum feed fractions containing asphaltic and oily constituents to lower boiling gaseous gasoline containing products which comprises: subjecting the feed fraction in a confined zone to contact with a porous inorganic oxide gel-type contact material consisting of particles having a greater average diameter than about .022 inch and having less than 30 percent of its pore volume taken up by pores having radii larger than about 100 Angstrom units, the remaining pore volume being taken up by smaller pores at a temperature below about 500° F., whereby the oily constituents of said feed fraction are substantially sorbed by said contact material and the asphalt constituents remain substantially unadsorbed, effecting a substantial separation of unadsorbed liquid from said contact material bearing sorbed oily constituents, passing said contact material downwardly through a confined conversion zone as a substantially compact column, introducing a preheated gas into the upper section of said conversion zone and passing it downwardly through said column to heat it to a temperature suitable for oxidation of said oily constituents, introducing an oxygen containing gas into said column at a plurality of levels along its length and passing said latter gas downwardly within said column to effect partial oxidation of a portion of the oily constituents with resultant liberation of heat, limiting the rate of oxygen introduction substantially to that required to heat said contact material and to maintain it at a temperature above about 750° F. which is suitable for conversion of said oily constituents to gaseous gasoline containing products, withdrawing said gaseous products from the lower section of said conversion zone, withdrawing used contact material bearing carbonaceous contaminant deposits from the lower end of said conversion zone substantially separately of said gaseous products, passing said used contact material through a confined regeneration zone while maintaining its temperature above the minimum level required for rapid burning of said deposits but below a heat damaging level, passing a combustion supporting gas into contact with said

contact material in said regeneration zone to burn said deposits, withdrawing the regenerated contact material from said regeneration zone, cooling said contact material to a suitable temperature below about 750° F. and reusing at least a portion of said contact material for contacting petroleum feed fraction as aforesaid.

14. A process for conversion of high boiling oily constituents in asphalt bearing hydrocarbon liquid feeds to lower boiling products which comprises: contacting said liquid feed for a suitable time and at a suitable temperature with a porous, particle-form contact material in which the pores are mostly micropores and the volume of the pores having radii larger than about 100 Angstrom units is less than about 30 percent of the total pore volume and in which the particles are of greater diameter than about 60 mesh size, to effect sorption of the oily constituents of said feed in the pores of said contact material while leaving substantially unsorbed the asphalt constituents, subjecting the contact material to washing with a suitable solvent to remove adhering asphalt containing liquid from the outer surface of said particles, passing the washed contact material bearing oily constituents through a confined zone as a substantially compact column of downwardly flowing particles, introducing an oxygen containing gas into said column at a plurality of vertically spaced intervals along its length to effect a partial oxidation of a portion of the sorbed oily constituents with resultant substantial heat liberation, controlling the rate of oxygen containing gas introduction to effect by said heat liberation the heating of said contact material to a temperature suitable for the conversion of said oily constituents to lower boiling products, withdrawing the lower boiling gaseous products from the upper section of said conversion zone and passing them through a second conversion zone in contact with a particle-form catalyst under suitable conversion conditions to effect further conversion of said gaseous hydrocarbons, withdrawing the used contact material bearing carbonaceous contaminant deposits from the lower end of said conversion zone substantially separately of said gaseous products, passing said used contact material through a confined regeneration zone while maintaining its temperature above the minimum level required for rapid burning of said deposits but below a heat damaging level, passing a combustion supporting gas into contact with said contact material in said regeneration zone to burn said deposits, withdrawing the regenerated contact material from said regeneration zone, cooling said contact material to a suitable temperature below about 750° F. and reusing at least a portion of said contact material for contacting petroleum feed fraction as aforesaid.

15. A process for conversion of the oily constituents in high boiling liquid hydrocarbon feeds containing asphaltic constituents to gaseous, gasoline containing products which comprises: maintaining within a confined de-asphalting zone a substantially compact column of contact material in the form of spheroidal siliceous gel par-

ticles characterized in that it consists substantially entirely of spheroidal contact material particles having an average diameter greater than about .022 inch and having less than 30 percent of its pore volume devoted to pores having radii larger than about 100 Angstrom units, the remaining pore volume being devoted to smaller pores, distributing said liquid feed onto said column adjacent its upper end and causing said liquid to pass downwardly within said column, while maintaining the temperature of said column below about 500° F., whereby oily constituents of said feed are sorbed by said contact material and the asphaltic constituents remain substantially unsorbed, withdrawing the contact material and unsorbed liquid from said deasphalting zone, draining the liquid from said contact material, subjecting the contact material to a quick wash with a suitable hydrocarbon solvent to wash from its outer surface adhering asphalt containing liquid, heating said washed contact material to a temperature suitable for oxidation of said oily constituents by oxygen and passing the contact material as a substantially compact column downwardly through a confined conversion zone, introducing oxygen into said column at a plurality of spaced levels along its length to effect partial oxidation of said oily constituents with resultant heat liberation, controlling the rate of oxygen introduction to effect heating of said contact material to and maintaining it at a temperature above about 750° F. which is suitable for conversion of the sorbed oily constituents to gaseous gasoline containing products, maintaining said oily constituents in contact with said heated contact material a sufficient time to effect said conversion, effecting separation of said gaseous products from the used contact material upon which a carbonaceous contaminant has been deposited during said conversion, contacting the contact material at suitable elevated regeneration temperatures with a combustion supporting gas to burn off said contaminant deposit, cooling the contact material to a temperature suitable for introduction into said deasphalting zone and passing the cooled contact material into the upper section of said deasphalting zone to replenish said column therein.

LOUIS P. EVANS.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
226,001	Riebeck	Mar. 30, 1880
1,278,023	Rosenbaum	Sept. 3, 1918
1,447,297	Day	Mar. 6, 1923
1,568,018	Forrest et al.	Dec. 29, 1925
2,351,793	Voorhees	June 20, 1944
2,382,755	Tyson	Aug. 14, 1945
2,437,222	Crowley, Jr. et al.	Mar. 2, 1948

OTHER REFERENCES

Allibone, "Journal of the Institute of Petroleum," vol. 27, pages 94-108 (1941).

Certificate of Correction

Patent No. 2,487,794

November 15, 1949

LOUIS P. EVANS

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 3, lines 73 and 74, strike out the words "structure corresponding to that of an inorganic oxide gel having a substantially uniform porosity" and insert the same after "having a" in line 42, same column; line 66, for "buxites" read *bauxites*; column 13, line 14, for "codnucted" read *conducted*; column 20, line 21, strike out "stitueents, subjecting the contact material to" and insert instead *boiling products, passing the contact material*;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 9th day of May, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,

Assistant Commissioner of Patents.