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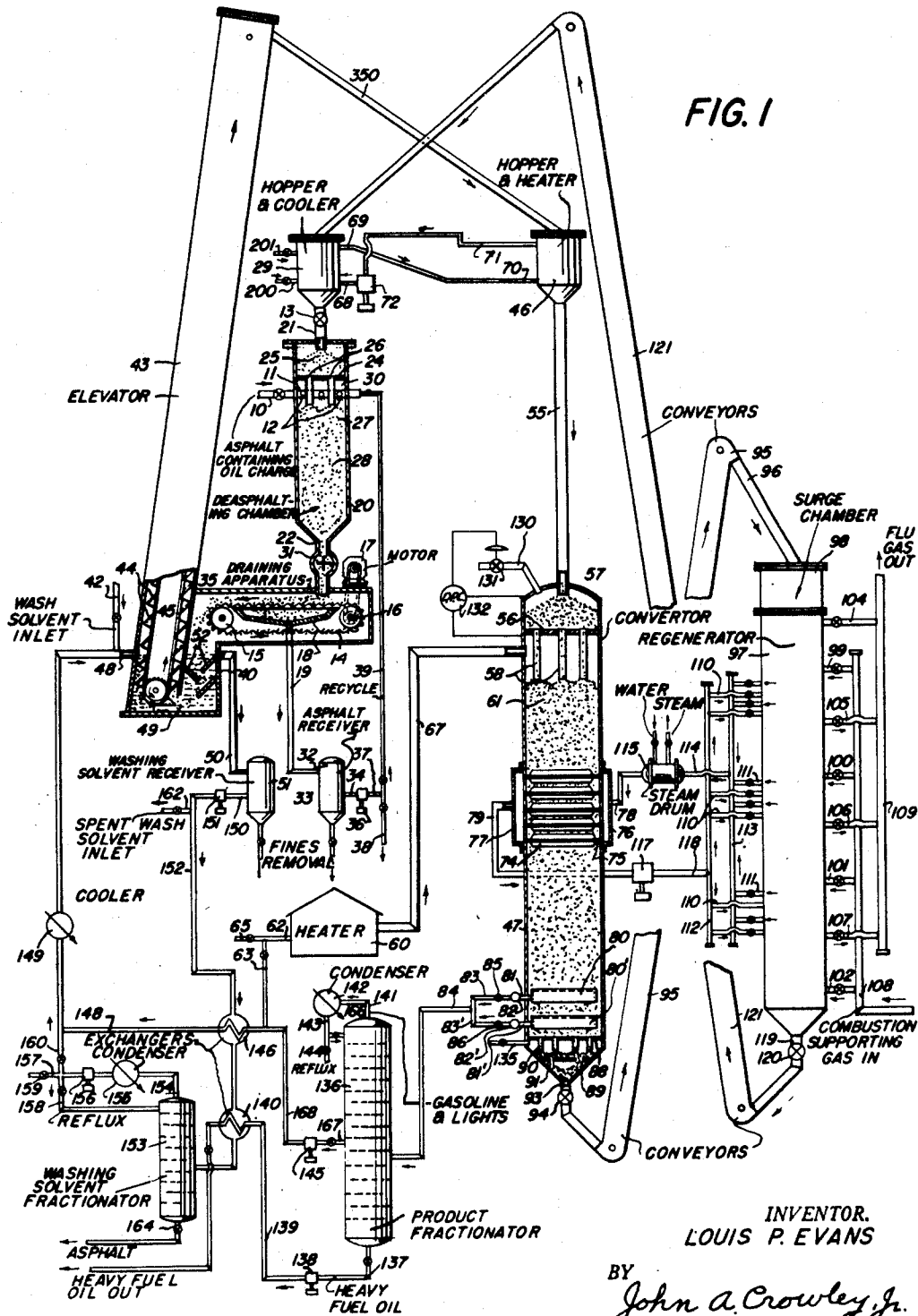
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HYDROCARBON CONVERSION PROCESS

Filed Feb. 6, 1948

2 Sheets-Sheet 1



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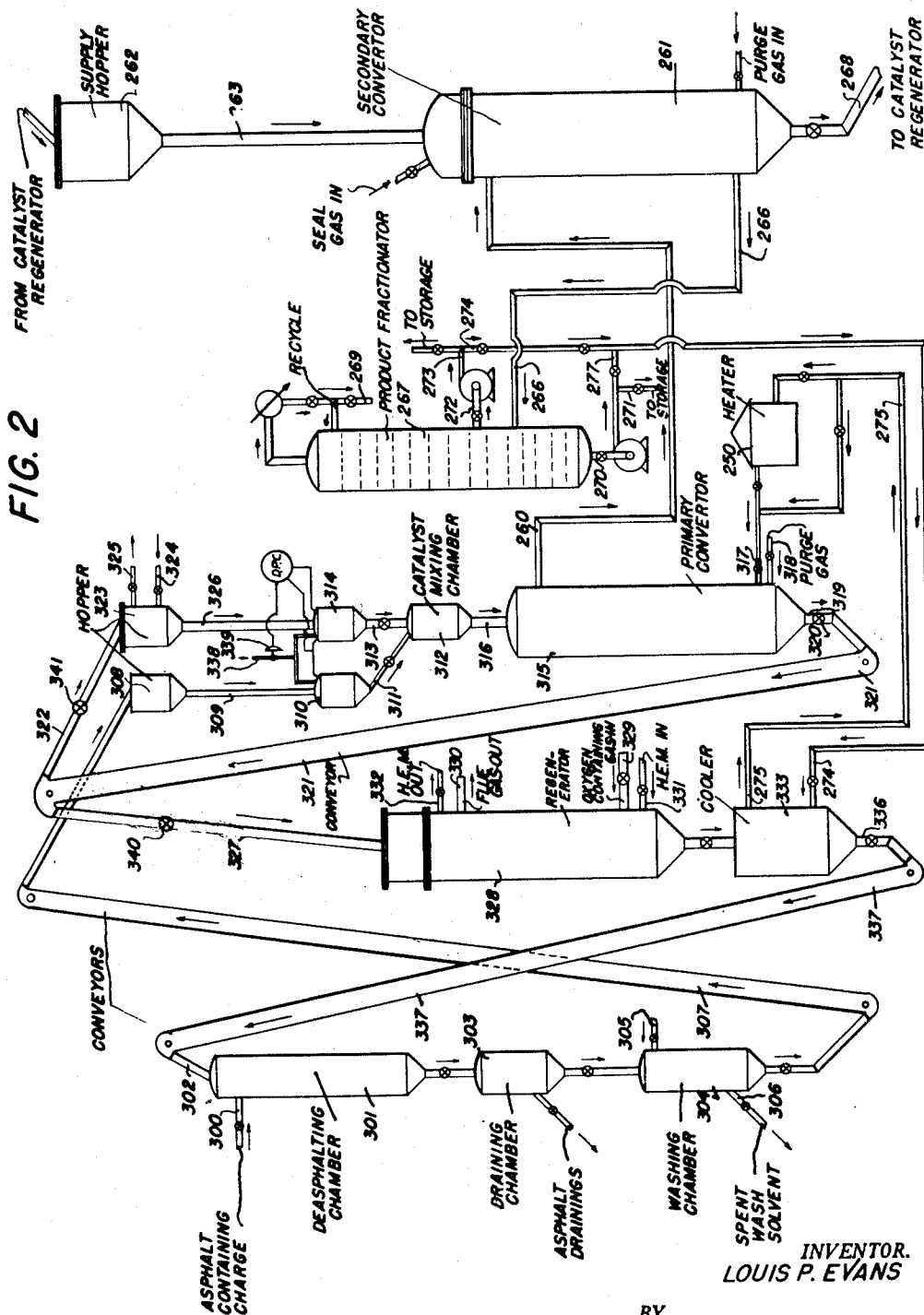
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2,487,796

HYDROCARBON CONVERSION PROCESS

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Application February 6, 1948, Serial No. 6,735

11 Claims. (Cl. 196—52)

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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 of hydrocarbon feed stocks which contain both asphaltic and oily constituents.

Such conversion processes may involve treating, reforming, polymerization, oxidation, desulfurization, cracking, etc., 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.

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 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

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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 high boiling asphalt bearing hydrocarbons which overcomes the above prior art difficulties is described and broadly claimed in my copending application Serial Number 720,271, filed in the United States Patent Office January 4, 1947 now abandoned. The process described in that application is broadly one wherein 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 unsorted the asphaltic constituents of the liquid feed. A substantial separation of unsorted 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 deals with certain improvements in the operation and method of heating the contact material bearing the oily constituents in the above mentioned process. According to one form of the instant invention the contact material is delivered into the conversion zone, below the desired hydrocarbon conversion temperature and is heated to the conversion temperature by passing a preheated vaporous charge stock or cycle stock through the conversion zone in contact with the contact material. The preheated vapor charge provides the heat required for its own conversion and also that required for the conversion and vaporization of the oily constituents sorbed on the contact material. The mixed gaseous products are withdrawn from the conversion zone together.

A major object of this invention is the provision of an improved process for conversion of high boiling asphalt bearing hydrocarbon frac-

tions 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 conversion.

Another object of this invention is the provision of a practical continuous cyclic process for the catalytic cracking conversion of petroleum residuums.

A specific object of this invention is the provision in a process wherein the oily hydrocarbon constituents from an asphalt bearing feed fraction are sorbed on a suitable sorbent material of an improved method for heating said sorbent material in the absence of non-sorbed asphalt material to accomplish the conversion of the sorbed oily constituents to lower boiling gaseous products.

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 combination deasphalting-cracking 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 structure corresponding to that of an inorganic oxide gel

the total pore volume and preferably 10 percent or less. The measurement of 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	2.3	5.1	2.3	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 Constituent 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 Per Cent.....			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 Per Cent.....		3.5	6.7		2.4	2.2	2.0

having a substantially uniform porosity of low macropore volume with an average pore diameter not exceeding about 125 Angstrom units and a particle size preferably not smaller than about 30 mesh for most operations, have the ability to sorb the oily constituents of a liquid hydrocarbon fraction while leaving substantially unsorbed the asphaltic constituents. Natural and treated clays and bauxites such as are employed in oil filtering and decoloring processes 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, those pores having radii larger than 100 Angstrom units, should constitute less than about 30 percent of

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 exhibited a preference for the oily constituents

over the asphaltic constituents. When the particle size was reduced below 60 mesh, the sorbent no longer preferentially adsorbed the oily 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, Hrs.....	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 Per Cent 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 coarser 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 of 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 absorbents 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, silica-magnesium oxide 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; and Figure 2 is a similar view of a modified arrangement. 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 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 into the washing chamber 40. The chamber 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 convertor 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, kero-

sene, benzol or light gas oil fraction may be introduced from an outside source through conduit 42 into 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 solvent receiver 51. 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 material 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 convertor supply hopper 46 into the upper end of convertor 47 as a substantially compact, elongated gravity feed leg flowing downwardly in conduit 55. Within the upper section convertor 47 a horizontal partition 56 is positioned so as to define a seal chamber 57 in the upper end of the convertor. 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 61 of contact material maintained in a lower section of the convertor. The relatively cool contact material bearing sorbed oily constituents is heated within the conversion zone by passage through the column 61 of hot preheated vaporous hydrocarbons introduced into the upper section of the conversion zone through conduit 67. The hydrocarbon vapors introduced at 67 may

consist of a gas oil or naphtha or normally gaseous hydrocarbons introduced from a point outside the system through pipe 65. The hydrocarbons so charged are heated in tubular heater 60 to a temperature above the desired conversion temperature in the convertor. The rate and temperature of the vapor hydrocarbon charge may be so controlled as to provide all the sensible and conversion heat required within the convertor. Preferably, the vaporous hydrocarbons introduced at 67 will consist of a gas oil cycle fraction recovered from the convertor products as will be discussed hereinafter. As the contact material and heated vaporous hydrocarbons pass downwardly through the convertor the temperature gradually rises to a suitable hydrocarbon conversion temperature after which it falls off somewhat in the lower part of the convertor. For example, the contact material may enter the convertor at 400° F., become heated to about 850-900° F. and pass from the bottom of the convertor at about 800° F.-850° F.

If desired, a portion of the required heat may be supplied to the conversion zone by means of heat supplied by indirect heat transfer with a suitable heat exchange fluid passing through the heat transfer tubes 75. The tubes 75 extend in spaced rows horizontally across vessel 47 below the lower ends of conduits 58 and are provided with attached fins 74 to enhance their surface area for heat transfer. An inlet manifold box 76 is provided on one side of the vessel to supply heat exchange fluid to the tubes 75 and an outlet manifold box 77 is provided on the opposite side of vessel 47. Heat exchange fluid enters box 75 through inlet conduit 78 and leaves box 77 through conduit 79. Any suitable heat exchange fluid such as superheated steam, flue gas or molten metallic alloys, lead or inorganic salts, etc. may be employed. As will be shown hereinafter a preferable source of the heat is the contact material regenerator.

After being heated to a suitable conversion temperature the oily constituents are catalytically converted to the desired gaseous products. The vaporous hydrocarbon charge introduced at 67 is also catalytically converted to lower boiling products, sufficient length of column 61 being provided below the level at which the contact material reaches the conversion temperature level to insure the desired amount of conversion. The mixed gaseous products 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. In the lower section of vessel 47, there are provided 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 mate-

rial 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 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. Heat transfer tubes or coils 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 connect into an outlet manifold 113.

As pointed out hereinabove 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 and steam drum 115 into conduit 78 and the manifold box 76 supplying the heat transfer tubes 75 in convertor 47. The heat exchange fluid after giving up its heat to the contact material in vessel 47 may then pass via manifold box 77, conduit 79, pump 117 and conduit 118 into the inlet manifold 112 which supplies the heat transfer tubes in the regenerator cooling stages through pipes 110. Any excess heat liberated by the contaminant burning over that supplied the contact material in convertor 47 may be removed by the evaporation of water to provide high pressure steam in drum 115. The heat exchange fluid may take any of a number of forms such as a suitable gas

under pressure or fused metallic oxides or mixture 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 where it is cooled to a temperature at which it may be reused in the deasphalting operation. The cooling may be accomplished by passage of a suitable heat exchange fluid, introduced at 200 and withdrawn at 201, in heat exchange relationship with the contact material in hopper 29. In a preferred form of the invention the heat exchange fluid introduced at 200 may consist of the cycle oil or virgin gas oil charge to the convertor which is partially preheated in heat transfer tubes within hopper 29 before its passage to the final heater 60 and then to the convertor 47. If desired, part of the heat removed from the contact material in hopper 29 may be employed in heating the contact material bearing sorbed oily constituents in hopper 46. In this event, additional 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. It will be noted that by means of the heat exchange tubes 75 within the convertor and the transfer of heat from the contact material to the vaporizable oil charge in hopper 29, a large portion of the heat obtained from contaminant combustion and from cooling the contact material to a suitable sorption temperature is recovered to supply the sensible heat and endothermic reaction heat requirements of the conversion step.

Considering again the gaseous products obtained from convertor 47 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 conversion products are directed by conduit 84 into a fractionator 136 which may be of the type conveniently used for this purpose. A heavy cycle or fuel oil fraction may be withdrawn from the bottom of the fractionator 136 through conduit 137. The fuel oil may be pumped by pump 138 through conduit 139 and through exchanger 140 whereby it is cooled. The cooled fuel oil may be withdrawn from the system or it may be recycled as part of the heavy liquid hydrocarbon feed to the de-

asphalting chamber 20. On the other hand the fuel oil if vaporizable without substantial coking may be passed through pipes 202, 168, 63 and 62 to heater 60 and then to convertor 47 through pipe 67. Gasoline and light products may be withdrawn from the top of fractionator 136 through conduit 141 through which it passes to condenser 142. Part of the condensed material may be refluxed via pipe 143 and 166 and part withdrawn via pipes 143 and 144 in order to be further treated and fractionated to provide a finished gasoline product. An intermediate boiling fraction or a light cycle oil boiling, for example, within the broad range about 400° F. to 800° F. may be withdrawn from an intermediate point along the fractionator 136 via conduit 167. This cycle oil may be pumped by pump 145 through conduit 168 to exchanger 146 wherein it is partially cooled. A portion of this cycle oil may be employed as the washing solvent for washing asphaltic material from the outer surface of the contact material particles in washing chamber 40. In case of such operation the cycle oil from exchanger 146 passes via conduit 148 through cooler 149, wherein it is adjusted to a suitable temperature for the washing operation and then into the boot section of elevator 43 via conduit 48. The cycle oil may entirely replace or merely supplement washing solvent from an external source introduced via conduit 42. Most of the light cycle oil is preferably passed via pipes 63 and 62 through heater 60, and thence to convertor 47 via conduit 67. As pointed out hereinabove, the cycle oil may be passed through heat transfer tubes within hopper 29 before entering the heater 60.

The used washing solvent collected in receiver 51 may be passed therefrom through conduit 150 to pump 151 and then via conduit 152 through exchangers 146 and 140 into a suitable solvent fractionator 153. In exchangers 146 and 140 the solvent is vaporized and heated to a suitable flash temperature for introduction into the fractionator 153. In fractionator 153 the washing solvent (i. e. cycle oil) is distilled from the asphaltic and high boiling material removed from the contact material in chamber 40. The asphalt containing liquid is withdrawn from the bottom of fractionator 153 through conduit 164 and the recovered solvent vapor is withdrawn from the top of fractionator 153 through conduit 154. The cycle oil vapors are condensed in condenser 155 and passed to pump 156. The condensate may in part be pumped through conduits 157 and 158 back to tower 153 as reflux, and part through conduits 157 and 159 to an outside storage. Alternatively part of the condensate may be passed through conduits 157 and 160 to conduit 148 to be reused as washing solvent.

Alternatively in some operations, the fractionator 153 may be eliminated and the used washing solvent containing asphaltic constituents may be withdrawn from the system through conduit 162 to be employed as a cutting stock in preparing refinery fuel blends and the like. This latter alternative is particularly feasible when a cycle gas oil is employed as the washing solvent. On the other hand, when an outside solvent such as a naphtha fraction is employed as the washing solvent, it is usually desirable to recover the solvent by fractionation.

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 unsorted 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 unsorted 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 unsorted 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 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 substantially 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, within 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 thereto 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 unsorted 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 of the deasphalting and sorbent washing system 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, spheroidal 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 un-sorbed 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. The catalyst bearing oily constituents was then heated to a temperature suitable for the cracking conversion of the sorbed oily constituents in a confined conversion zone. An analysis of the sorbed oily constituents before conversion was as follows:

A. P. I. gravity, 17.1
Viscosity (K. V.) at 210° F., 46
Pour point above 120° F.
Conradson carbon residue 5.7% by weight

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 to 1000° F. being preferred where gasoline is the desired product. Where non-condensable gases are the principal desired product 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 ratio of sorbed liquid oil to vaporized charge passed through the reactor is subject to considerable latitude because of the ability to vary the inlet temperature of both the contact material and the vaporized oil charge. However, the amount of vaporized charge should be limited to such an extent that space velocity in liquid volumes of sorbed liquid charge plus vapor charge (calculated at 60° F.) is not more than about 10 and preferably less than about 5 times the catalyst containing convertor volume in the conversion zone.

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.

It will be observed that in the above described modification of the invention the hydrocarbon vapor charge moves downwardly through the convertor concurrently with the contact material flow so that both the vapor charge and the sorbed oily constituents upon vaporization must pass through a substantial length of contact material column before leaving the convertor. Thus usually in concurrent flow operation the vaporized oily constituents are adequately contacted with catalyst after vaporization to insure the optimum conversion yields. Where adequate contact is not provided and particularly in countercurrent flow operations, it has been found desirable to pass the mixed gaseous products from the initial convertor through a second convertor to contact fresh hot catalyst and thereby obtain complete conversion. Such a modified process is shown in Figure 2. In the arrangement shown in Figure 2 the asphalt bearing liquid charge is introduced via conduit 300 into deasphalting chamber 301 wherein it is contacted with inorganic oxide gel-type contact material particles which are introduced at a suitable temperature through duct 302. The contact material and un-sorbed asphalt containing liquid then pass into chamber 303 wherein they are separated. The contact material is then washed in chamber 304 with a suitable solvent introduced at 305 and withdrawn at 306. The washed contact material is then transferred by conveyor 307 to hopper 308 from which it flows through a gravity feed leg 309 to seal chamber 310. The contact material

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passes via conduit 311 from seal chamber 310 to mixing chamber 312 wherein it is mixed with hot, at least partially spent contact material entering chamber 312 via conduit 313 from seal chamber 314. The mixed contact material passes at a suitable conversion temperature into the top of convertor 315 via conduit 316. Gaseous conversion products are withdrawn from the convertor via conduit 260 and spent contact material bearing a carbonaceous contaminant, after being purged by a suitable gas introduced into chamber 315 at 318, is withdrawn from the bottom of convertor 315 via conduit 319 at a rate controlled by valve 320.

A preheated vaporized cycle oil is introduced into the lower section of convertor 315 from heater 250 via conduit 317. This vaporized charge passes upwardly through the column of catalyst in convertor 315 and heats it to a suitable temperature for conversion of the sorbed liquid hydrocarbons. Both the vaporized charge and the sorbed liquid hydrocarbons are catalytically converted to lower boiling products existing in the gaseous phase and these products pass from the upper section of the convertor via conduit 260 into the secondary convertor 261. Freshly regenerated catalyst which may or may not be similar in nature to that used in convertor 315 is supplied from hopper 262 through leg 263 into convertor 261 at a suitable conversion supporting temperature. The hydrocarbons pass down through a column of catalyst in chamber 261 to become finally converted and the conversion products pass from the lower section of convertor 261 via conduit 266 to a conventional product fractionator 267. The used catalyst from convertor 261 is withdrawn via conduit 268 and is then passed to a separate regenerator (not shown). Gasoline and lighter products are withdrawn from the fractionator 267 through conduit 269. A heavy fuel oil is withdrawn from the bottom of the fractionator through conduit 270 and may then be pumped to storage via conduit 271. A light cycle oil boiling below about 800° F., for example, is withdrawn from the fractionator at 272 and pumped via pipes 273 and 274 to heat transfer tubes within catalyst cooler 333. The oil is partially preheated in these tubes and then passes via pipe 275 to heater 250 wherein it is further heated to a temperature substantially above the desired average conversion temperature in convertor 315. For example, where the average conversion temperature in convertor 315 is about 850° F., the vaporized cycle stock may enter through conduit 317 at about 900–1000° F. or even higher. Care should be taken however to avoid substantial pyrolytic cracking within the tubes of heater 250. In some operations sufficient heat may be recovered from the catalyst in cooler 333 to permit by-passing of heater 250. In some cases when the fuel oil recovered at 270 is of a nature permitting vaporization and heating to the required temperature without substantial pyrolytic conversion, the fuel oil may be passed via conduit 277 to conduit 274 and thence through the preheaters to the convertor 315 along with the lighter cycle stock.

Considering again the primary convertor 315, since the gas flow is countercurrent to the catalyst flow, the catalyst temperature is highest at the catalyst discharge end of the convertor. In order to recover some of the heat removed in the spent catalyst, a portion of the spent contact material is transferred via conveyor 321 to chute

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322, feeding the hopper 323. The hot contact material passes from hopper 323 via feed leg 325 to mixing chamber 314 wherein it mixes with and partially heats the cooler oily constituent bearing contact material from the deasphalting system. If desired the contact material in hopper 323 may be further heated before passing to the mixing chamber by passage of air there-through at controlled rates to burn off a sufficient portion of the contaminant deposit to heat the spent catalyst to the desired pre-mixing temperature. The air may be introduced into hopper 323 via pipe 324 and combustion gases may be withdrawn via pipe 325. The remainder of the spent contact material from convertor 315 is transferred via conveyor 321 to chute 327, feeding to the regenerator 328 wherein it is substantially completely regenerated by means of air or oxygen, etc., introduced at 329 and withdrawn at 330. A suitable cooling fluid may be introduced through conduit 331 to suitable heat transfer tubes (not shown) within the regenerator in order to control the contact material temperature below a heat damaging level during the contaminant burning. The cooling fluid may be withdrawn from the heat transfer tubes via conduit 332. The regenerated contact material passes from regenerator 328 to cooler 333 wherein it is cooled by means of the cycle stock passed through the heat transfer tubes therein. The cooled contact material passes from cooler 333 via conduit 336 and is transferred by conveyor 337 to conduit 302 feeding the deasphalting chamber 301. An inert gas, such as steam, may be supplied to seal chambers 310 and 314 through conduit 338 at a rate controlled by valve 339 sufficient to maintain an inert gaseous pressure in both seal chambers above the gaseous pressure in catalyst mixing chamber 312. The relative amounts of spent catalyst passing from conveyor 321 to regenerator 328 and to hopper 323 may be controlled by means of valves 340 and 341 on chutes 327 and 322 respectively. Alternatively two separate conveyors may be used at this point in the system.

In a typical operation, contact material bearing sorbed oily constituents may be introduced into mixing chamber 312 at about 300° F. and mixed with sufficient amount of spent catalyst from hopper 323, existing at about 900° F. to provide a convertor mixed catalyst inlet temperature of about 600–750° F. In general the proportions of catalyst from hoppers 310 and 314 which are mixed to form the stream entering the convertor through conduit 316 should be regulated so that the catalyst enters the convertor at a temperature above the condensation temperature of the hydrocarbon products which are to be withdrawn through conduit 260. The amount of inert purge gas such as steam or flue gas introduced into the convertor at 318 or if desired along with the vapor charge at 317, may be regulated to control the condensation temperature of the mixed vapor stream withdrawn at 260. The mixed catalyst after entering the convertor then gradually rises to a peak temperature of about 925° F., near the bottom of the convertor. In the secondary convertor a temperature within the range about 850–1000° F. may be maintained.

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: contacting the asphalt-containing fraction with a porous particle-form contact material in which most of the pores are micropores and the volume of the pores having radii greater than about 100 Angstrom units is less than about 30 percent of the total pore volume, controlling the relationship between the contact time and temperature and of the size of the pores in said contact material to effect the sorption of the oily constituents of said fraction in the pores of said contact material while the asphalt constituents remain substantially unsorbed, effecting a substantial separation of the contact material bearing sorbed oily constituents from the unsorbed material and heating said contact material to a temperature suitable for the desired conversion of said oily constituents by passing a preheated hydrocarbon vapor boiling substantially below said oily constituents into contact with said contact material.

2. A process for conversion of oily constituents present in liquid fractions containing oily and asphalt constituents at elevated temperatures which comprises: contacting the asphalt-containing fraction with a porous particle-form contact material of larger than about 60 mesh size 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 at a temperature below about 500° F. whereby the oily constituents of said fraction are sorbed in the pores of said contact material while the asphalt constituents remain substantially unsorbed effecting a substantial separation of the contact material bearing sorbed oily constituents from the unsorbed material and heating said contact material to a temperature suitable for the desired conversion of said oily constituents by passing a preheated hydrocarbon vapor boiling substantially below said oily constituents into contact with said contact material, effecting a separation of the gaseous conversion products from the used contact material and passing said conversion products into contact with fresh particle-form contact material at an elevated conversion temperature to effect further conversion thereof.

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 macropores is less than about 30 percent of the total pore volume and in which the particles are coarser 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 the contact material to a temperature suitable for the conversion of said oily constituents to lower boiling products, separating said lower boiling products from said contact material, recovering a cycle fraction boiling sub-

stantially below said sorbed oily constituents from said products, preheating said cycle fraction to a temperature substantially above the suitable conversion temperature for said sorbed oily constituents and passing said preheated cycle fraction into contact with said contact material bearing the sorbed oily constituents to supply at least a substantial portion of the heat required for heating said contact material as aforesaid.

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 period below about 10 hours and at a temperature below about 500° F. 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 of greater than about 100 Angstrom units is less than about 30 percent of the total pore volume and in which the particles are coarser 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; heating the contact material to a temperature suitable for the conversion of said oily constituents to lower boiling products separating said lower boiling products from said contact material, and passing a hydrocarbon vapor boiling substantially below the sorbed oily constituents, preheated to a temperature above said conversion temperature into contact with said contact material to supply at least a major portion of the heat required for the heating of said contact material and for effecting the conversion of said sorbed oily constituents.

5. 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 of 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 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, passing the separated contact material through a confined zone while heating it therein to a temperature suitable for effecting the conversion of said oily constituents to lower boiling products; preheating a hydrocarbon feed fraction boiling below said sorbed oily constituents to a temperature substantially above the conversion temperature for said sorbed oily constituents, passing said preheated feed in the gaseous phase through said confined zone in contact with the contact material to effect conversion of said preheated feed and to supply at least a substantial portion of the heat required for heating said contact material as aforesaid; effecting a substantial separation of the mixed fluid conversion products from the contact material which bears a carbonaceous contaminant deposit; effecting the removal of said contaminant deposit from said contact material and re-using the contact material after removal of said

contaminant deposit for contacting said liquid asphalt bearing feed as aforesaid.

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 of 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 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 unsorted; draining the unsorted 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 heating it to a temperature suitable for the conversion of said oily constituents to lower boiling products; preheating a separate hydrocarbon feed boiling below the sorbed oily constituents to vaporize the same and heat it to a temperature substantially above the average conversion temperature in said confined zone; passing said preheated feed in the gaseous phase through said confined zone in contact with said contact material at a rate sufficient to supply at least a major portion of the heat required for heating said contact material as aforesaid; effecting separation of the gasiform conversion products from the used contact material and passing the separated gasiform products through a second confined zone in contact with a freshly regenerated particle-form catalytic material at a suitable conversion temperature to effect further conversion of said products to a final gasoline containing product.

7. 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 which are greater than 100 Angstrom units in radius, 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 unsorted, effecting a substantial separation of unsorted liquid from said contact material bearing sorbed oily constituents, passing said contact material downwardly through a confined conversion zone as a substantially compact column while heating it to 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, separating a cycle fraction boiling below said sorbed oily constituents from said gaseous products, preheating said cycle fraction to a temperature above the average conversion tempera-

ture in said conversion zone, passing said preheated cycle fraction in the gaseous phase downwardly through said column in said conversion zone at a rate sufficient to supply at least a major portion of the heat required for heating said contact material as aforesaid and for effecting conversion of said cycle fraction and said sorbed oily constituents to lower boiling products, 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.

8. 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 0.22 inch and having less than 30 percent of its pore volume taken up by pores of greater than 100 Angstrom units radius, the remaining pore volume being taken up by smaller pores, controlling the contacting 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 unsorted, effecting a substantial separation of unsorted liquid from said contact material bearing sorbed oily constituents, passing said contact material downwardly through a confined conversion zone as a substantially compact column, preheating a separate hydrocarbon fraction boiling substantially below said sorbed oily constituents to vaporize and heat the same to a temperature substantially above that required for its conversion in the presence of said contact material, passing said preheated fraction upwardly through said column counter-currently to the solid flow in said conversion zone to heat said contact material to a temperature above about 750° F. suitable for the conversion of said preheated fraction and said sorbed oily constituents to lower boiling gasiform products, withdrawing the mixed gasiform products from the upper section of said conversion zone and passing said products through a second confined conversion zone in contact with suitable freshly regenerated contact material at a suitable conversion temperature above about 750° F. to effect further conversion of said products to gasiform gasoline containing products, withdrawing used contact material bearing a carbonaceous contaminant deposit from the lower section of said first conversion zone, 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.

9. A process for conversion of the oily constituents present in a liquid hydrocarbon feed containing both oily and asphaltic constituents at elevated temperatures which process comprises the steps: contacting said liquid feed in a confined zone 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 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; passing said contact material bearing sorbed oily constituents through a confined conversion zone as a substantially compact column to effect conversion of said oily constituents to gaseous products; withdrawing said gaseous products from said conversion zone; withdrawing used contact material bearing a carbonaceous contaminant deposited during said conversion from said conversion zone substantially separately of said gaseous products; passing said used contact material through a confined regeneration zone and contacting it therein with a combustion supporting gas to burn said contaminant; passing a suitable heat exchange fluid in indirect heat transfer relationship with the contact material in said regeneration zone to remove the excess heat released by the contaminant burning so as to prevent the contact material from rising to a heat damaging level during regeneration; passing the heat exchange fluid from the regeneration zone in indirect heat transfer relationship with the contact material in said conversion zone to supply a portion of the heat required to heat said contact material and sorbed oily constituents to a suitable temperature for effecting said conversion of said oily constituents; preheating a hydrocarbon gas oil fraction boiling substantially below said sorbed oily constituents to a temperature above the desired average hydrocarbon conversion temperature; passing said preheated gas oil fraction as a vapor through said column in said conversion zone to effect its conversion to lower boiling products and to supply the remainder of the heat required to heat said contact material and sorbed oily constituents to a suitable hydrocarbon conversion temperature; withdrawing regenerated contact material from said regeneration zone; cooling said regenerated contact material to a suitable temperature below about 750° F. for contacting said asphalt containing liquid feed and reusing the cooled contact material for sorbing oily constituents from said liquid feed as aforesaid.

10. A process for conversion of the oily constituents present in a liquid hydrocarbon feed containing both oily and asphaltic constituents at elevated temperatures which process comprises the steps: contacting said liquid feed in a confined zone 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 of greater than about 100 Angstrom units is less than about 30 percent of

the total pore volume and in which the particles are substantially larger 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; passing said contact material bearing sorbed oily constituents through a confined conversion zone as a substantially compact column while heating it to a temperature suitable for effecting conversion of said oily constituents to gaseous products; withdrawing said gaseous products from said conversion zone, withdrawing used contact material bearing a carbonaceous contaminant deposited during said conversion from said conversion zone substantially separately of said gaseous products; passing said used contact material through a confined regeneration zone and contacting it therein with a combustion supporting gas to burn said contaminant while controlling the contact material temperature below a heat damaging level, passing a hydrocarbon fraction boiling below said sorbed oily constituents in indirect heat transfer relationship with the hot regenerated contact material to cool the contact material to a suitable temperature below about 750° F. for contacting said asphalt containing liquid feed and to pre-heat said hydrocarbon fraction; passing the preheated hydrocarbon fraction at a temperature above that required for conversion of said sorbed oily constituents through the column in said conversion zone to supply at least a substantial portion of the heat required to heat said contact material as aforesaid; and reusing the cooled contact material for sorbing oily constituents from said liquid feed as aforesaid.

11. A process for the conversion of oily constituents present in asphalt bearing high boiling liquid hydrocarbon fractions which comprises: contacting the asphalt bearing fraction with a particle-form contact material of substantial particle size as distinguished from powdered contact material said contact material being of a pore structure wherein less than 30 percent of the total pore volume is occupied by pores of greater than about 100 Angstrom unit radius, controlling the relationship between particle diameter and the contacting time and temperature to effect the sorption of the oily constituents of said fraction in the pores of said contact material particles while leaving substantially unsorbed the asphalt constituents, effecting a substantial separation of the unsorbed liquid from the contact material particles bearing the sorbed oily constituents, mixing said contact material bearing sorbed oily constituents with a stream of hot contaminant bearing contact material to partially heat toward a temperature suitable for the conversion of said sorbed oily constituents, passing said mixed contact material as a substantially compact column downwardly through a confined conversion zone, preheating a hydrocarbon fraction boiling below said sorbed oily constituents to a temperature above that required for conversion of said oily constituents, passing said preheated fraction upwardly through said column in said conversion zone to heat it to the temperature required to effect conversion of said sorbed oily constituents to lower boiling products, withdrawing gasiform conversion products from the upper section of said conversion zone, withdrawing hot contaminant bearing contact material from the lower

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section of said conversion zone, using a portion of said hot contaminant bearing contact material for admixture with said oily constituent bearing contact material as aforesaid, passing the remaining portion of said contaminant bearing contact material from said conversion zone through a confined regeneration zone to substantially remove said contaminant deposit therefrom, adjusting the temperature of the regenerated contact material and utilizing it for contacting asphalt bearing liquid hydrocarbons as aforesaid.

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