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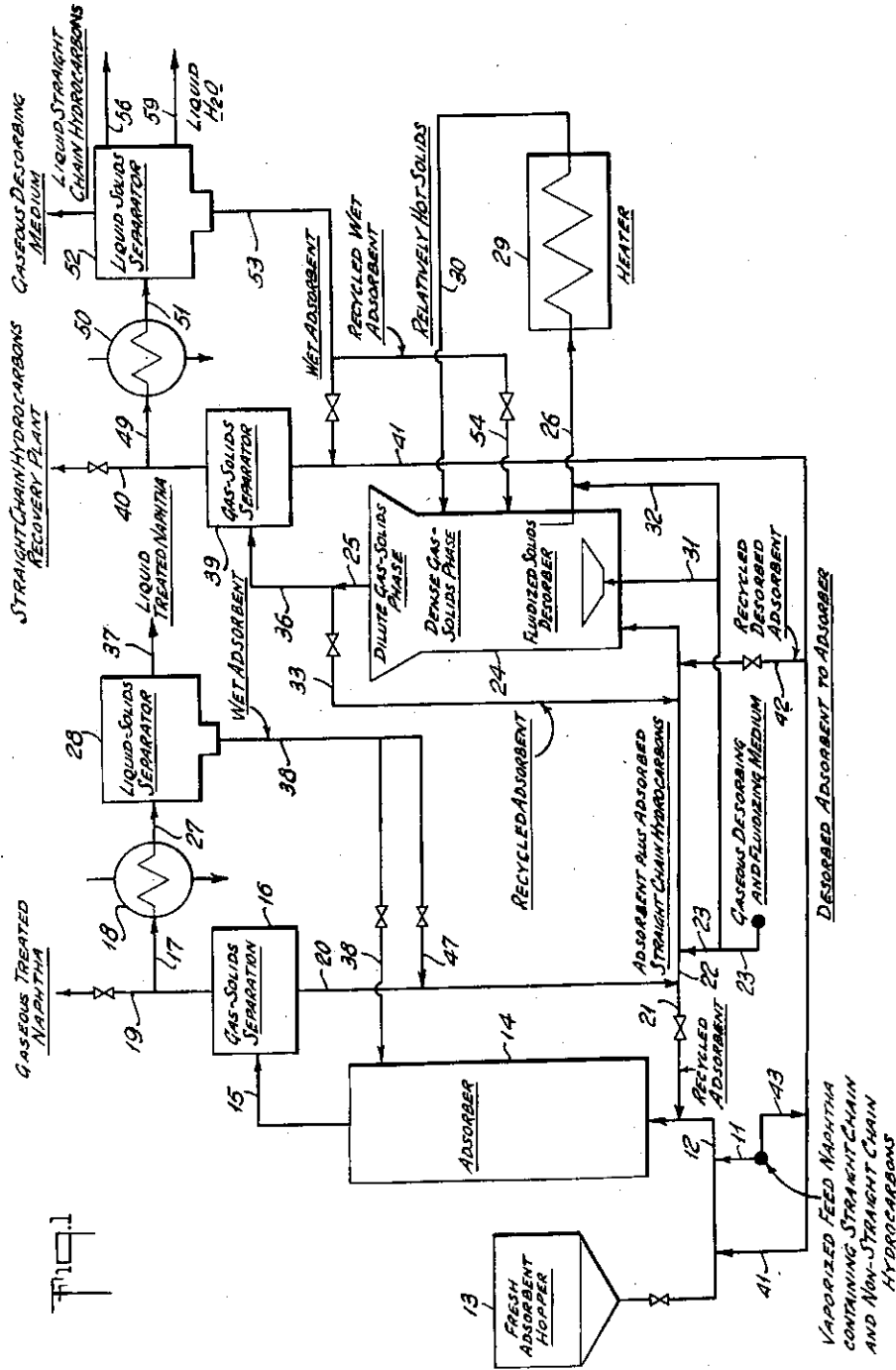
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METHOD OF TREATING HYDROCARBONS

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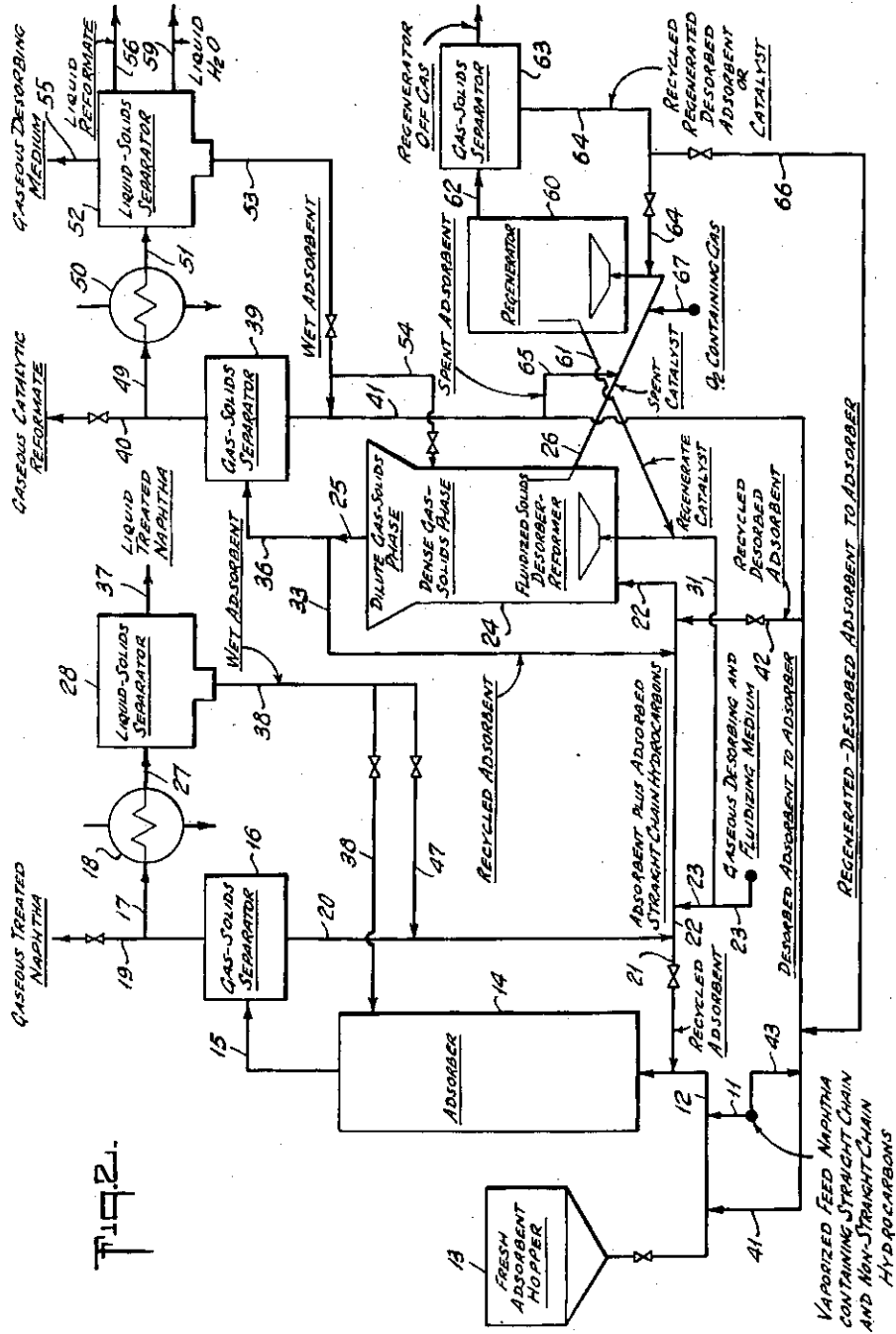
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METHOD OF TREATING HYDROCARBONS

Samuel P. Dickens, Port Arthur, Benjamin F. Smith, Grove, and Wiley P. Ballard, Port Arthur, Tex., assignors to The Texas Company, New York, N. Y., a corporation of Delaware

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9 Claims. (Cl. 208-85)

This invention relates to a method of treating hydrocarbon fractions, such as petroleum fractions and hydrocarbon synthesis (Fischer-Tropsch) fractions. In accordance with one embodiment this invention relates to the treatment of hydrocarbon fractions in the naphtha or gasoline boiling range, said fractions containing straight chain and non-straight chain hydrocarbons, in order to improve their quality. In accordance with still another embodiment this invention relates to an improved hydrocarbon conversion process. Generally this invention is directed to the upgrading of petroleum fractions containing straight chain and non-straight chain hydrocarbons, especially naphtha stocks wherein the amount of straight chain hydrocarbons is substantial, e. g. in the range 2-30% by volume and higher.

Accordingly, it is an object of this invention to provide an improved process for treating hydrocarbon fractions containing straight chain hydrocarbons and non-straight chain hydrocarbons.

It is another object of this invention to provide a flexible hydrocarbon converting process which is capable of handling a wide variety of hydrocarbon fractions containing straight chain hydrocarbons and non-straight chain hydrocarbons.

Another object of this invention is to provide a combination hydrocarbon treating process for treating a hydrocarbon fraction containing straight chain hydrocarbons and non-straight chain hydrocarbons wherein the straight chain hydrocarbons are selectively adsorbed by means of a solid selective adsorbent, followed by desorption of the straight chain hydrocarbons in a special manner in accordance with this invention.

Still another object of this invention is to provide a combination hydrocarbon treating process wherein a hydrocarbon fraction containing straight chain hydrocarbons and non-straight chain hydrocarbons can eventually be converted substantially entirely to non-straight chain hydrocarbons.

In at least one embodiment of this invention at least one of the foregoing objects will be achieved.

How these and other objects of this invention are achieved will become apparent with reference to the accompanying disclosure and drawings wherein:

Fig. 1 schematically illustrates one embodiment of the practice of this invention employing a desorption zone containing fluidized solids, and

Fig. 2 schematically illustrates another embodiment of the practice of this invention employing in combination an adsorption operation followed by a substantially simultaneous desorption and catalytic reforming of the components adsorbed during the adsorption operation.

In accordance with our invention we have provided an improved process for treating or converting a hydrocarbon fraction containing straight chain hydrocarbons and non-straight chain hydrocarbons which comprises subjecting the hydrocarbon fraction to be treated to contact with a selective adsorbent which selectively adsorbs

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straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons from said fraction, separating from the aforesaid adsorption operation a treated effluent having a reduced straight chain hydrocarbon content and said solid adsorbent containing straight chain hydrocarbons adsorbed therein and entraining the resulting separated solid adsorbent in a gaseous or vaporous desorbing medium whereby said entrained adsorbent is carried into contact with a mass of solid particle-form contact material under conditions of temperature and flow such that the straight chain hydrocarbons are desorbed from the solid adsorbent while at the same time the solid adsorbent is elutriated through the mass of solid contact material. Following desorption and elutriation of the solid adsorbent there is separately recovered a gas-solids phase comprising the gaseous desorbing medium, the resulting gaseous desorbed straight chain hydrocarbons together with the regenerated solid adsorbent entrained therein, thereby effecting a separation between the solid adsorbent and the solid particle form contact material. At this point it is mentioned that the separation of the solid adsorbent from the solid particle-form contact material by elutriation is due primarily to the substantial difference in average particle size between the solid adsorbent, which is relatively small, and the solid particle-form contact material, which is relatively large.

By straight chain hydrocarbons is meant any aliphatic or acyclic or open chain hydrocarbon which does not possess side chain branching. Representative straight chain hydrocarbons are the normal paraffins and the normal olefins, mono- or polyolefins, including the straight chain acetylenic hydrocarbons. The non-straight chain hydrocarbons comprise the aromatic and naphthenic hydrocarbons as well as the isoparaffinic and isoolefinic hydrocarbons and the like. Straight chain hydrocarbon-containing mixtures which are suitably treated in accordance with this invention include the various petroleum fractions, such as a naphtha fraction, a gasoline fraction, a diesel oil fraction, a kerosene fraction, a gas oil fraction and the like. Particularly suitable for treatment in accordance with this invention are straight chain hydrocarbon-containing fractions having a boiling point or a boiling range in the range 40-600° F. and higher and containing a substantial amount of straight chain hydrocarbons, e. g. 2-35% by volume. More particularly, a petroleum fraction suitable for use in the practice of this invention might have an initial boiling point in the range 40-300° F. and an end point in the range 150-600° F. Furthermore a petroleum fraction suitable for use in the practice of this invention must contain both straight chain and non-straight chain hydrocarbons and might have the following composition:

Hydrocarbon Type	Percent by Volume
Naphthenes.....	0-75
Aromatics.....	0-50
Acyclic Saturates (including normal paraffins and isoparaffins).....	2-90
Acyclic Unsaturates (including normal olefins and isoolefins).....	0-50

Typical refinery stocks or fractions which are applicable to the practice of this invention are a wide boiling straight run naphtha, a light straight run naphtha, a heavy straight run naphtha, a catalytic cracked naphtha, a thermally cracked or thermally reformed naphtha, a catalytic reformed naphtha and the like.

Any solid selective adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons can be

employed in the practice of this invention. It is preferred, however, to employ as the selective adsorbent certain natural or synthetic zeolites or aluminosilicates, such as a calcium aluminosilicate, which exhibit the property of a molecular sieve, that is matter made up of porous crystals wherein the pores of the crystals are of molecular dimension and are of substantially uniform size. A particularly suitable solid adsorbent for straight chain hydrocarbons is a calcium aluminosilicate, apparently actually a sodium calcium aluminosilicate manufactured by Linde Air Products Company and designated Linde Type 5A Molecular Sieve. The crystals of this particular calcium aluminosilicate have a pore size or diameter of about 5 Angstrom units, a pore size sufficiently large to admit straight chain hydrocarbons, such as the normal paraffins and normal olefins, to the substantial exclusion of the non-straight chain naphthenic, aromatic, isoparaffinic and isoolefinic hydrocarbons. This particular selective adsorbent is available in various sizes. One form of the above-mentioned selective adsorbent, Type 5A Molecular Sieve, is available as a finely divided powder having a particle size in the range 0.5-5.0 microns, exhibiting a bulk density in lbs. per cubic foot of 33, and a particle density in grams per cc. of 1.6.

Other suitable solid selective adsorbents include the synthetic and neutral zeolites which, when dehydrated, may be described as crystalline zeolites having a rigid three dimensional anionic network and having interstitial dimensions sufficiently large to adsorb straight chain hydrocarbons but sufficiently small to exclude non-straight chain hydrocarbons possessing larger molecular dimensions. The naturally occurring zeolites, chabazite, exhibits such desirable properties. Another suitable naturally occurring zeolite is analcite $\text{NaAlSi}_3\text{O}_8 \cdot \text{H}_2\text{O}$, which, when dehydrated, and when all or part of the sodium is replaced by an alkaline earth metal, such as calcium, by base exchange yields a material which may be represented by the formula $(\text{Ca}, \text{Na})\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$ and which, after suitable conditioning, will adsorb straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons. Naturally occurring or synthetically prepared phacolite, gmelinite, harmotome and the like or suitable base exchange modifications of these zeolites are also suitable.

Other solid inorganic or mineral selective adsorbents are known and may be employed in the practice of this invention. It is contemplated that selective adsorbents having the property of selectively adsorbing straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons in the manner of a molecular sieve may be obtained by suitable treatment of various oxide gels, especially metal oxide gels of the polyvalent amphoteric metal oxides.

The adsorptive separation of the straight chain hydrocarbons from the hydrocarbon fraction undergoing treatment may be carried out in the liquid or gaseous phase and at any suitable temperature and pressure effective in the adsorptive separation operation. It is desirable, of course, to coordinate the adsorptive separation conditions, e. g. such as temperature and pressure with the desorptive separation conditions described hereinafter so as to effect a most economical use of the materials employed and for ease of control.

The adsorptive separation of the straight chain hydrocarbons by the solid selective adsorbent may be carried out at any suitable temperature such as a temperature in the range 50-1000° F. and at any suitable pressure such as a pressure in the range 0-10,000 p. s. i. g. and higher, the temperature and pressure being adjusted with respect to the hydrocarbon fraction undergoing treatment depending upon whether or not it is desired to maintain the hydrocarbon fraction in the liquid phase or in the vapor phase during the adsorptive separation operation. Liquid phase adsorption may be carried out

by simply slurring the solid adsorbent with the liquid hydrocarbon fraction to be treated, followed by separation or decantation of the treated hydrocarbon effluent now substantially free of or having a reduced straight chain hydrocarbon content. Liquid phase adsorption may also be carried out by percolating the liquid hydrocarbon fraction to be treated through a bed of solid adsorbent material. It is preferred, however, in the practice of this invention to carry out the adsorptive separation operation in the gaseous phase, that is to maintain the hydrocarbon fraction undergoing treatment in the vapor phase during the adsorptive separation operation. Any suitable method for effecting gas-solid contact may be employed, for example a fixed bed, a moving bed or a fluidized bed of selective adsorbent may be employed during gas phase adsorptive separation. It is preferred in the practice of this invention to employ a finely divided solid selective adsorbent such as a sodium calcium aluminosilicate as exemplified by the Linde Type 5A Molecular Sieve, having a particle size distribution in the range 0.5-5.0 microns and to entrain the adsorbent to the gaseous hydrocarbon fraction undergoing treatment. After a sufficient contact time, the entrained solid adsorbent is separated from the gaseous treated effluent now having a reduced amount of straight chain hydrocarbons. The separated solid adsorbent is then subsequently treated to desorb the straight chain hydrocarbons therefrom.

The desorption of straight chain hydrocarbons from the solid adsorbent material can be made at any suitable temperature or pressure. For example, the desorption operation may be carried out at a pressure in the range 0-10,000 p. s. i. g. Generally a desorption pressure in the range 10-2,000 p. s. i. g. is suitable. It is sometimes desirable to carry out the desorption operation at a pressure substantially lower than the adsorption pressure. In general, the pressure employed during the adsorptive separation operation is not determinative of the desorption pressure and any suitable desorption pressure may be employed. Substantially the same comments may be made with respect to the desorption temperature.

Generally any suitable desorptive temperature may be employed in the practice of this invention. It is sometimes desirable, however, to carry out substantially isothermal adsorption-desorption operations. Any suitable desorption temperature in the range 400-1100° F., higher or lower, may be employed. It is preferred, however, to carry out the desorption operation at an elevated temperature such as a temperature in the range 700° F.-1100° F. It is realized, of course, that the desorption temperature should not be excessively high, for example not greater than about 1100°-1300° F., in the case of Linde Type 5A Molecular Sieve, which excessive temperatures would lead to destruction of the adsorbent material, presumably by collapse of the crystal structure, with resultant loss of its selective adsorption properties.

Although it is possible to effect desorption of the straight chain hydrocarbons from the solid adsorbent by the application of heat alone, for example by radiant heating or by indirect heat exchange, it is a feature of this invention that the desorption operation is carried out in the presence of a gaseous desorbing medium within which the selective adsorbent undergoing desorption or regeneration is entrained. Generally any suitable gaseous desorbing medium may be employed in the practice of this invention. As a general rule, however, it is preferred to employ a gaseous desorbing medium the molecules of which are sufficiently small so that penetration of the pores of the adsorbent may be effected. The following materials may be employed as the gaseous desorbing medium: nitrogen, methane, hydrogen, carbon dioxide, carbon monoxide, flue gas, substantially dry natural gas (mixture of methane and ethane) and the like including

air under controlled temperature conditions, and steam, preferably superheated steam. In general, any vaporizable material which possesses a high heat capacity, is thermally stable and which is readily separable, as by distillation or condensation, from the desorbed straight chain hydrocarbons may be used.

During the desorption of the straight chain hydrocarbons from the entrained powdery solid adsorbent the adsorbent is at the same time elutriated through a mass of solid contact material under conditions such that the desorbing medium together with the desorbed straight chain hydrocarbons and the entrained solid adsorbent pass through the interstices of the mass of solid contact material and are separated therefrom. The mass of solid contact material may comprise a fixed bed, a moving or falling bed or a fluidized bed of solid particle-form contact material. This solid particle form contact material serves to maintain the desorption operation at the desired desorption temperature. Additionally, besides serving as a means to control the desorption temperature, the solid contact material also tends to aid the desorption of the straight chain hydrocarbons from the adsorbent by promoting contact between the adsorbent and desorbing medium, such as by increasing residence time and the like. The solid contact material may serve as a means for effecting desorption temperature control in the following manner. For example, in the instance when the gaseous desorbing medium, also employed to entrain the solid adsorbent, is initially at a relatively high temperature, e. g. 700° F. or above about 700° F., upon introduction of the desorbing medium together with treated solid adsorbent into the desorption zone which contains solid particle-form contact material the desorption operation can be conveniently carried out at a temperature lower than about 700° F. by supplying and maintaining in the desorption zone relatively cool solid particle-form contact material. Alternatively, should it be desired to maintain the desorption operation, i. e. the desorption zone, at a relatively elevated temperature, e. g. above about 700° F., while at the same time introducing into the desorption zone the gaseous desorbing medium together with the entrained adsorbent at a temperature below 700° F., e. g. 500° F., the solid contact material is maintained or introduced into the desorption zone at a relatively elevated temperature, such as above about 700° F. Accordingly in view of the foregoing it is apparent that, depending upon the temperature of the desorbing medium together with entrained adsorbent with respect to the solid particle-form contact material, the solid particle-form contact material may serve as a means for cooling or heating the desorbing medium. If desired the solid contact material may be maintained at a rather high temperature during the desorption operation, sufficiently high, preferably not higher than 1300° F., to effect thermal cracking of the desorbed straight chain hydrocarbons. In the instance where the solid particle-form contact material is introduced or maintained in the desorption zone at substantially the same temperature as the gaseous desorbing medium the solid contact material serves substantially only to provide a more efficient desorption operation by promoting more intimate and vigorous contact between the desorbing medium and the solid contact material being elutriated therethrough.

The solid particle-form contact material provided in the desorption zone may comprise any substantially inert, solid thermophore such as a non-metal or metal or their oxides, or refractory ceramic material, in the form of granular particles, pellets, balls, etc. When the contact material is in the form of a porous fixed bed the mass of contact material should be sufficiently permeable so that the powdery adsorbent material can be readily elutriated therethrough. If desired, the solid contact material may be in the form of a fluidized bed, fluidization of the solid contact material conveniently being effected by the desorbing medium flowing therethrough.

In accordance with one embodiment of the practice of this invention the solid contact material possesses cracking activity with respect to straight chain hydrocarbons, that is, it comprises a cracking catalyst such as a silica-alumina cracking catalyst. When a cracking catalyst is employed as the solid contact material or as a component thereof and when the desorption operation is carried out at a suitable elevated temperature, e. g. above 800° F., not only are the straight chain hydrocarbons desorbed but substantially simultaneously with the desorption operation the straight chain hydrocarbons are cracked to form corresponding low molecular weight hydrocarbons and corresponding olefinic or unsaturated hydrocarbons. Suitable cracking catalysts are well known to those skilled in the art and generally comprise aluminosilicates. Cracking catalysts are available in various forms and sizes, e. g. pellets, beads, microspheres and the like. In the practice of this invention the cracking catalyst employed should have an average particle size substantially greater than the average particle size of the adsorbent material, so that the adsorbent material can be readily elutriated through the mass of cracking catalyst when the cracking catalyst is maintained in a fixed bed, a moving or falling bed or a fluidized bed. In the fluidized system satisfactory results are obtainable when the cracking catalyst or solid particle-form contact material has an average particle size greater than about 200 mesh.

In accordance with still another feature of this invention the solid particle form contact material is desirably a material which exhibits catalytic reforming activity, that is a reforming or isomerization catalyst. Reforming catalysts are well known and comprise such materials as a platinum-containing catalyst, a cobalt molybdate catalyst, so-called Hyperforming catalyst, chromia-alumina catalyst which may be identified as a Sovaforming or Thermoform catalytic reforming catalyst, a molybdena-alumina catalyst sometimes referred to as a Hydroforming or Orthoforming catalyst and the like. During reforming the desorbed straight chain hydrocarbons undergo substantially simultaneously a number of reactions including isomerization, dehydrogenation, aromatization or dehydrocyclization, cracking, disproportionation, and the like depending upon the severity of the desorbing-reforming conditions and the composition of the desorbed straight chain hydrocarbons. It is apparent in view of the foregoing that when the solid contact material comprises a reforming or isomerizing catalyst simultaneous desorption and reforming or isomerization of the straight chain hydrocarbons is accomplished. Generally straight chain hydrocarbon reforming or isomerization operations are carried out at a temperature in the range 750-1100° F. and at a pressure in the range 40-1,000 p. s. i. g., more or less, desirably in the presence of hydrogen. The severity of the reforming or isomerization operation is dependent to some extent upon the composition of the desorbed straight chain hydrocarbons and the quality or composition of the catalytic reformate desired. Usually during the reforming operation there is a net production of hydrogen (due to dehydrogenation of the hydrocarbons) which advantageously is subsequently separated from the resulting effluent and employed as a desorbing medium as well as the means for elutriating the powdery adsorbent through the reforming catalyst.

Referring now to the drawing and in particular to Fig. 1 thereof which schematically illustrates one embodiment of the practice of this invention as applied to the treatment of a hydrocarbon naphtha fraction, a light straight run naphtha having a boiling range in the range 45-250° F. and containing straight chain hydrocarbons and non-straight chain hydrocarbons is supplied in vaporized form via line 11 into conduit 12 which is supplied with powdery solid adsorbent material, Linde Type 5A Molecular Sieve, from hopper 13. In conduit 12 the vaporized naphtha fraction fluidizes and entrains the

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powdery adsorbent and carries the same into adsorber or adsorption zone 14. Adsorption zone 14 may comprise one or more vessels or conduits of sufficient size such that the residence time or contact time between the adsorbent material and the naphtha fraction is such that there issues from adsorber 14 via line 15 a gas-solids phase containing solid adsorbent having straight chain hydrocarbons adsorbed therein together with a gaseous naphtha fraction substantially free or having a reduced straight chain hydrocarbon content. The gas-solids phase in line 15 is introduced into a gas-solids separator 16 wherein the solid adsorbent is separated from the resulting treated gaseous effluent which is removed via line 19. The gas-solids separator 16 may comprise a cyclone, a Cottrell precipitator, ceramic filter, bag filter or combinations of the above to effect substantially complete separation of the solid adsorbent from the gas stream. The separated solid adsorbent is removed from the gas-solids separator 16 via line 20. If desired, depending upon operating conditions within the adsorber, a portion of this removed adsorbent may be recycled to adsorber 14 via line 21 to effect a substantially complete separation of the straight chain hydrocarbons from the naphtha fraction introduced into adsorber 14. The above-described adsorption operations are carried out at substantially atmospheric pressure and at a temperature in the range 50-550° F.

When the powdered adsorbent is made up of finely divided particles, as in the case of Linde Type 5A Molecular Sieve which has a particle size in the range 0.5-5.0 microns, all of the adsorbent sometimes will not be recovered by the gas-solids separator 16 alone. In order to recover the more finely divided adsorbent which remains entrained in the treated effluent or naphtha leaving separator 16 via line 19, the treated effluent is passed via line 17 through condenser 18 to cool and condense the treated naphtha and then through line 27 into liquid-solids separator 28 from which the liquid treated naphtha, substantially free of adsorbent, is removed via line 37. The separated adsorbent, wetted by the treated naphtha is removed from liquid-solids separator 28 via line 38 for recycle to adsorber 14 or for introduction via line 47 into relatively hot, dry adsorbent in line 20. Liquid-solids separator 28 may comprise a baffled tower or hold-up settling tank, alone or in combination with a liquid-solids filter, suitable to effect separation of solids from liquid.

The solid adsorbent material, containing straight chain hydrocarbons adsorbed therein removed from separator 16 via line 20 is contacted in line 22 with a gaseous desorbing medium comprised predominantly of methane introduced into line 22 by means of line 23. The gaseous desorbing medium, methane, entrains the solid adsorbent material within line 22 and introduces the same into a fluidized solids desorber or desorption zone 24 which also contains a fluidized mass of relatively inert solid particle-form contact material, such as solid metal particles or balls or abrasion-resistant refractory pebbles, the gaseous desorbing medium serving to elutriate the entrained adsorbent material through the fluidized bed of contact material and at the same time serving to fluidize said contact material. Because of the great difference in particle size between the adsorbent material, which possess a particle size in the range 0.5-5.0 microns, and the contact material which has a particle size greater than 200 mesh, the solid adsorbent material, after intimate contact with the desorbing medium and solid contact material within desorption zone 24 is elutriated therethrough and removed as a relatively dilute gas-solids phase from the top of desorber 24 via line 25. Desorber 24 is maintained at an effective desorption temperature in the range 700-800° F. by introducing the desorbing medium, methane, at substantially that temperature. The desorption operation is endothermic and accordingly the heat of desorption must be supplied. The heat of desorption

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is advantageously supplied in accordance with this invention by continuously withdrawing a portion of the fluidized solid contact material from within desorber 24 by means of line 26 passing the same to heat exchanger 29 wherein its temperature is increased sufficiently so that when it is returned to desorber 24 via line 30 sufficient heat is available therein to maintain the desorption operation of desorber 24 at the desired desorption temperature. As indicated in Fig. 1 a portion of the desorbing medium is desirably introduced into desorber 24 by means of line 31 to aid in fluidization of the solid contact material therein and another portion is desirably introduced by means of line 32 into line 26 in order to effect movement of the solid contact material through line 26, heater 29 and line 30 back into desorber 24.

The relatively dilute gas-solids phase issuing from desorber 24 via line 25 comprises the gaseous desorbing medium, methane, the resulting gaseous desorbed straight chain and the desorbed-regenerated adsorbent. If desired a portion of the whole relatively dilute gas-solids phase may be recycled to the desorber 24 via line 33 in order to better effect control of the desorption operation. The whole relatively dilute gas-solids phase is withdrawn from line 25 via line 36 and introduced into gas-solids separator 39 to effect separation of the desorbed-regenerated adsorbent from the gas stream which is withdrawn via line 40 and passed to a straight chain hydrocarbon recovery plant for separation of the straight chain hydrocarbons from the methane desorbing medium. The separation of the desorbed straight chain hydrocarbons from the methane desorbing medium may be effected by charcoal adsorption and the like, the methane desorbing medium being separately recovered and recycled to desorber 24.

As previously indicated with respect to the operation of gas-solids separator 16, if a substantial amount of adsorbent remains entrained in the gas phase issuing via line 40 from gas-solids separator 39, the gas stream is introduced via line 49 into cooler-condenser 50 for condensation of the normally liquid desorbed hydrocarbons and then via line 51 into liquid-solids separator 52. A liquid stream comprising substantially only straight chain hydrocarbons is recovered from separator 52 via line 56, provision also being made for the recovery of the gaseous desorbing medium via line 55 and for the withdrawal of liquid water (condensed steam) via line 59 in the event steam is employed as the desorbing medium. The solid adsorbent, separated in liquid-solids separator 52, now wetted by the liquefied straight chain hydrocarbons and/or water, is withdrawn via line 53 for admixing with the previously separated dry adsorbent in line 41 or, if desired, for recycle to desorber 24 via line 54.

The resulting desorbed-regenerated adsorbent is removed from gas-solids separator 39 via line 41 and recycled to adsorber 14 via line 12 to contact additional fresh naphtha feed. If desired a portion of the solid adsorbent recovered from gas-solids separator 39 and present in line 41 may be recycled to desorber 24 via line 42. As indicated fresh naphtha feed is injected into line 41 by means of line 43 in order to effect movement or transfer of the desorbed-regenerated adsorbent eventually to adsorber 14.

Referring now in detail to Fig. 2 of the drawing which schematically illustrates another feature of the practice of this invention wherein a reforming catalyst is employed as said solid particle-form contact material such that the desorption and reforming operations are carried out substantially simultaneously, that is catalytically reforming the straight chain hydrocarbons almost as soon as they are desorbed from the solid adsorbent. For reasons of simplicity and ease of understanding, the same reference numerals employed with respect to Fig. 1 are also used in Fig. 2 to identify substantially the same apparatus and conduits.

Briefly, Fig. 2 schematically illustrates an operation wherein straight chain hydrocarbons are adsorbed from a naphtha fraction in a gas phase adsorption system, followed by separation of the adsorbent containing straight chain hydrocarbons adsorbed therein, thereby yielding a naphtha effluent having a reduced straight chain hydrocarbon content or substantially free of straight chain hydrocarbons. The resulting adsorbent material is contacted with a gaseous desorbing medium, hydrogen, and entrained therein and introduced into a desorption zone which is provided with a fluidized bed of reforming catalyst, e. g. a so-called Hydroforming or Orthoforming catalyst, wherein the straight chain hydrocarbons are desorbed from the adsorbent and reformed in the presence of the reforming catalyst. A stream of spent reforming catalyst is withdrawn from the combination desorber-reformer and introduced into a catalyst regeneration zone wherein any carbon deposited upon the reforming catalyst is burned off by contact with air. The resulting hot regenerated reforming catalyst is returned to the combination desorber-reformer. At the same time there is produced overhead from the combination desorber-reformer a relatively dilute gas-solids phase comprising the stripping medium, hydrogen, gaseous catalytic reformate comprising straight chain and non-straight chain hydrocarbons, and the desorbed-regenerated adsorbent which is eventually recycled into the aforementioned adsorption zone. The desorbed-regenerated adsorbent is separately recovered and recycled to the adsorber, the resulting catalytic reformate being separately recovered from the hydrogen desorbing medium. If desired a portion of the recovered catalytic reformate may be recycled to the adsorption zone for the removal of straight chain hydrocarbons therefrom.

Referring now in greater detail to Fig. 2 a naphtha fraction which may be higher boiling than or substantially the same as disclosed with respect to Fig. 1, is introduced via line 11 into conduit 12 wherein it contacts and entrains powdered solid adsorbent, e. g. Linde Type 5A Molecular Sieve, supplied to conduit 12 via hopper 13. The gaseous naphtha fraction containing entrained solid adsorbent enters adsorber or adsorption zone 14 wherein at least a substantial amount of straight chain hydrocarbons originally present in the naphtha fraction are adsorbed by the adsorbent. There issues from adsorber 14 via line 15 a gas-solids phase containing resulting treated naphtha fraction now having a reduced straight chain hydrocarbon content and containing entrained solid adsorbent. This gas-solids phase enters gas-solids separator 16 wherein substantially all or a substantial amount of the adsorbent is separated via line 20. The remaining treated naphtha effluent may be separately withdrawn via line 19 or introduced by means of line 17 into cooler or condenser 18 to liquefy the treated naphtha fraction which is transferred via line 27 into a liquid-solids separator 28 for the removal of any remaining solid adsorbent. A liquid treated naphtha effluent substantially free of adsorbent is removed via line 37. This treated effluent is substantially free of straight chain hydrocarbons. Any solid adsorbent removed in liquid-solids separator 28 is recycled to adsorber 14 via line 38 and/or introduced into line 20 via line 47.

The separated solid adsorbent removed from separator 16 via line 20 is introduced into line 22 wherein it is contacted by gaseous desorbing medium, hydrogen, introduced thereto via line 23. The resulting entrained adsorbent together with the hydrogen is introduced into combination desorber-reformer 24 wherein is maintained a fluidized bed of hydroforming catalyst such as a so-called Orthoforming catalyst comprising a molybdena-alumina catalyst maintaining a minor amount, e. g. 9-11% by weight, MoO₃. This reforming catalyst is maintained as fluidized bed within desorber-reformer 24 by the injection thereto of gaseous hydrogen via line 31. Because of the great difference in average particle size

between the entrained solid adsorbent introduced into the combination adsorber-reformer via line 22 and the fluidized reforming catalyst therein, the solid adsorbent is elutriated through the mass of fluidized reforming catalyst and there issues overhead from adsorber-reformer 24 via line 25 a relatively dilute gas-solids phase containing gaseous hydrogen and gaseous catalytic reformate containing entrained solid adsorbent. If desired a portion of this whole gas-solids phase may be recycled to adsorber-reformer 24 via line 33.

The whole gas-solids phase issuing from adsorber-reformer 24 via line 25 is introduced via line 36 into gas-solids separator 39 wherein a substantial portion of the desorbed-regenerated entrained adsorbent is separated and removed via line 41. The gas phase separated from gas-solids separator 39 is introduced via line 49 in cooler or condenser 50. The resulting cooled mixture now containing gaseous hydrogen, liquefied catalytic reformate and any entrained solid adsorbent is introduced via line 51 into liquid-solids separator 52 wherein the entrained solid adsorbent material is removed via line 53. This removed solid adsorbent may be directly introduced into desorber-reformer 24 via line 54 or into line 41 which contains desorbed-regenerated adsorbent separated from gas-solids separator 39. Gaseous hydrogen is removed from separator 52 via line 55 and desirably it is recycled to desorber-reformer 24 as the desorbing medium. Liquid reformate is removed from separator 52 via line 56. If desired this liquid reformate, containing straight chain and non-straight chain hydrocarbons is recycled to adsorber 14 in order to remove the straight chain hydrocarbons therefrom. Provision is made for the separate withdrawal from separator 52 by means of line 59 of liquid water in the event that steam or superheated steam is employed together with hydrogen as the desorbing medium.

As is apparent in Fig. 2 provision has been made for the regeneration of spent reforming catalyst. In accordance with this embodiment a stream of spent reforming catalyst is withdrawn from adsorber-reformer 24 by means of line 26 and introduced into catalyst regenerator 60 wherein it is contacted and fluidized by means of incoming oxygen-containing stream such as air introduced into regenerator 60 via line 67. Within catalyst regenerator which is operated at a suitable catalyst regeneration temperature such as a temperature in the range 800-1200° F. substantially all of the carbon which may have been deposited upon the reforming catalyst is burned. The resulting regenerated reforming catalyst is removed from catalyst regenerator 60 and introduced into adsorber-reformer 24 via line 61. Provision is made for the recovery of any catalyst fines entrained in the regenerated off-gas or flue gas by means of line 62, gas-solids separator 63 and recycle line 64.

It has been observed in actual practice that after the solid adsorbent material has undergone a number of adsorption-desorption operations, particularly when relatively high desorption temperatures are employed (desorption temperatures in the range 600-1100° F.), carbon is deposited upon the solid adsorbent material with the result that its adsorptive capacity is adversely affected. In accordance with this invention provision is made for the intermittent or continuous regeneration of the desorbed adsorbent issuing from adsorber-reformer 24 by the withdrawal of a side stream of a solid adsorbent of 24 via line 65 and introducing the same into regenerator 60 wherein carbon is burned therefrom. The regenerated adsorbent is removed from regenerator 60 via line 62 and separated in gas-solids separator 63 and returned via lines 64 and 66 to line 41 for eventual introduction into adsorber 14.

In accordance with still another feature of this invention the reforming catalyst regeneration and the regeneration of the spent adsorbent may be carried out substantially simultaneously within regenerator 60 by

elutriating the solid adsorbent through the fluidized mass of catalyst undergoing regeneration in regenerator 60, in a manner similar to the operation adsorber-reformer 24, the small amount of catalyst fines which may be introduced into the regenerator adsorbent stream issuing from regenerator 60 via line 62 being considered negligible.

Although, with respect to Fig. 2, the practice of this invention has been illustrated wherein a so-called orthoforming or hydroforming molybdena-alumina catalyst is employed, it is pointed out that any suitable catalyst which effects the desired conversion or treatment of the desorbed straight chain hydrocarbons, for example, a platinum-containing reforming or isomerizing catalyst such as the platforming catalyst or ultraforming catalyst may be employed. Also a cracking catalyst or a dehydrogenation-aromatization catalyst such as a catalyst containing chromia, alumina and magnesia.

Further illustrative of the practice of this invention a mixture of straight chain hydrocarbon comparable to the mixture of straight chain hydrocarbons released or desorbed within desorber 24 and comprising 23% by volume n-pentane, 56% by volume n-hexane and 21% by volume n-heptane was contacted with a particle-form dehydrogenation-aromatization catalyst comprising Cr_2O_3 - MgO - Al_2O_3 at various temperatures and at a space velocity of about 0.4 v./hr./v. at a pressure of about 40 p. s. i. g. and at a H_2 recycle rate of 1200 cu. ft./bbl. of feed. The properties of the resulting up-graded product are set forth in Table No. I.

Table No. I

Temp., °F.....	920	943
Wt. percent recovery.....	93.8	81.3
Bromine No.....	20	22
Vol. percent aromatics.....	15	13
ASTM Res. Clear Oct. Prod.....	60.6	57.6
+3 cc. TEL/gal.....	80.4	80.2

Likewise, the same mixture of straight chain hydrocarbons was contacted with a number of platinum-containing reforming or predominantly isomerizing catalysts at a pressure of about 500 p. s. i. g., a H_2 recycle rate of about 4000 cu. ft./bbl. charge. The results are set forth in Table No. II.

Table No. II

Temp., °F.....	800			850			900		
	A	B	C	A	B	C	A	B	C
Catalyst.....									
P. D. Gas Make.....	0.209	0.173	0.150	0.414	0.338	0.299	2.567	2.609	0.715
Liq. Rec., Wt. Percent.....	95.9	99.3	90.1	95.0	98.0	88.2	67.7	70.1	72.7
Isomate ASTM Res., Clear.....	60.0	51.0	54.0	75.4	74.0	77.1	89.6	70.0	78.9
Finished ASTM Res., Clear.....	78.0	81.0	72.0	84.0	82.0	82.6		80.3	
Finished, +3 cc. TEL/gal.....		86.0							

A—Platforming catalyst.
B—Standard Baker Rd 150 catalyst.
C—Ultraforming catalyst.

For purposes of simplicity and clarity, conventional control equipment, valves, pumps, compressors, heaters, coolers and supplementary gas-liquid gas-solids and liquid-solids separators, fractionators, etc. have for the most part not been illustrated in the drawings. The location and employment of these auxiliary pieces of equipment such as may be necessary in the practice of this invention are well known to those skilled in the art.

As is evident to those skilled in the art many modifications, substitutions and changes are possible in the practice of this invention without departing from the spirit or scope thereof.

We claim:

1. A method of treating a hydrocarbon stream con-

taining straight chain hydrocarbons and non-straight chain hydrocarbons which comprises contacting said stream with a solid particle-form selective adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons therefrom, thereby producing a treated effluent having a reduced amount of straight chain hydrocarbons, separating said solid adsorbent, now containing straight chain hydrocarbons adsorbed therein, from said treated effluent, contacting said separated solid adsorbent with a gaseous desorbing medium in the presence of a porous fixed mass of particle-form catalytic material under conditions to effect desorption of said straight chain hydrocarbons from said adsorbent and catalytic conversion of the resulting desorbed straight chain hydrocarbons whereby the resulting regenerated adsorbent together with the converted desorbed straight chain hydrocarbons and gaseous desorbing medium pass through the interstices of said fixed bed of catalyst, recovering from the aforementioned desorption-conversion operation a relatively dilute gas-solids phase comprising converted hydrocarbons, gaseous desorbing medium and said regenerated adsorbent substantially free of said catalyst, and separating said adsorbent from said dilute gas-solids phase.

2. A method in accordance with claim 1 wherein a portion of said converted hydrocarbons, after separation of the regenerated adsorbent therefrom, is recycled to contact said first-mentioned hydrocarbon stream for the removal of straight chain hydrocarbons therefrom.

3. A method of treating a gaseous stream containing straight chain hydrocarbons and non-straight chain hydrocarbons which comprises contacting said stream with a particle-form selective adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons therefrom, thereby producing a gaseous treated effluent and having a reduced amount of straight chain hydrocarbons and containing said adsorbent entrained therein, separating said solid adsorbent from said treated effluent, entraining said separated adsorbent in a gaseous desorbing medium and passing the same into contact with a fluidized mass of reforming catalyst under conditions such that the straight chain hydrocarbons are desorbed from said solid adsorbent

and are catalytically reformed by contact with said fluidized catalyst, elutriating the resulting regenerated adsorbent from said fluidized mass of catalyst together with said gaseous desorbing medium and the resulting reformed straight chain hydrocarbons, separately withdrawing a portion of the catalyst from said fluidized bed, regenerating the same and returning the resulting regenerated catalyst to said fluidized bed.

4. A method in accordance with claim 3 wherein said gaseous desorbing medium comprises predominantly hydrogen.

5. A method of treating a hydrocarbon stream containing straight chain hydrocarbons and non-straight chain hydrocarbons which comprises contacting said stream with a solid particle-form selective adsorbent

which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons therefrom, thereby producing a treated effluent having a reduced amount of straight chain hydrocarbons and containing said solid adsorbent entrained therein, separating said solid adsorbent from said treated effluent, contacting said separated solid adsorbent with a gaseous desorbing medium in the presence of a fluidized mass of reforming catalyst under conditions to effect desorption of said straight chain hydrocarbons from said adsorbent and catalytic reforming of the resulting desorbed straight chain hydrocarbons whereby the resulting regenerated adsorbent together with the reformed desorbed straight chain hydrocarbons and gaseous desorbing medium pass through said fluidized bed of reforming catalyst, recovering from the aforementioned desorption-reforming operation a dilute gas-solids phase comprising reformed hydrocarbons, gaseous desorbing medium and said regenerated adsorbent and substantially free of said reforming catalyst, separating said adsorbent from said dilute gas-solids phase, recycling at least a portion of said separated regenerated adsorbent to contact said first-mentioned hydrocarbon stream, recovering said reformed straight chain hydrocarbons, separately withdrawing spent reforming catalyst from said fluidized bed to a catalyst regeneration zone wherein it is contacted with an oxygen-containing stream to regenerate said withdrawn catalyst and recycling the resulting regenerated catalyst to said fluidized bed.

6. A method of treating a gaseous hydrocarbon stream containing straight chain hydrocarbons and non-straight chain hydrocarbons which comprises contacting said gaseous stream with a particle-form selective adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons therefrom under conditions whereby said particle-form adsorbent is entrained in said gaseous hydrocarbon stream, separating said solid adsorbent now containing straight chain hydrocarbons adsorbed therein from the resulting gaseous efflu-

ent now having a reduced amount of straight chain hydrocarbons therein, contacting and entraining said solid adsorbent in a gaseous desorbing medium and passing the resulting relatively dilute gas-solids phase into contact with a relatively dense gas-solids phase containing a fluidized mass of solid particle-form reforming catalyst maintained as a fluidized bed by said gaseous desorbing medium, the desorption contacting operation being carried out under conditions to effect desorption of said straight chain hydrocarbons from said adsorbent and catalytic reforming of the resulting desorbed straight chain hydrocarbons by said reforming catalyst, elutriating the resulting regenerated adsorbent from said fluidized mass of reforming catalyst by means of said gaseous desorbed medium together with the gaseous resulting reformed hydrocarbons, separately recovering said regenerated adsorbent from said gaseous reformed hydrocarbons and said gaseous desorbing medium and recycling the separated adsorbent to the aforesaid adsorption contacting operation.

7. A method in accordance with claim 6 wherein said reforming catalyst is a chromia-alumina reforming catalyst.

8. A method in accordance with claim 6 wherein said reforming catalyst is a molybdena-alumina reforming catalyst.

9. A method in accordance with claim 6 wherein said catalyst is a platinum-containing reforming catalyst.

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