Jan. 12, 1960 R. N. FLECK ET AL 2,921,026

FRACTIONATION PROCESS

Filed July 13, 1956 3 Sheets-Sheet 1

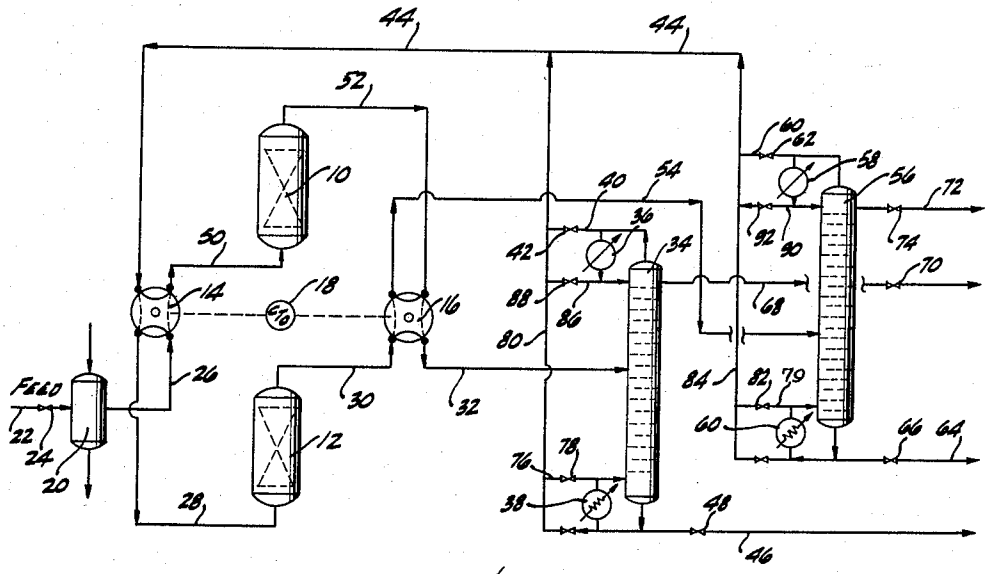


FIG. 1.

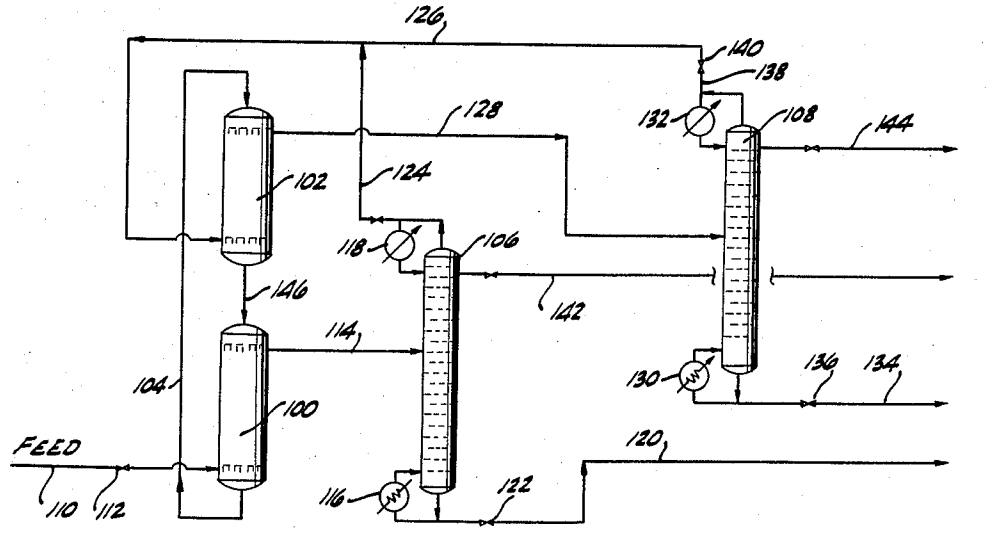


FIG. 2.

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FRACTIONATION PROCESS

Filed July 13, 1956 3 Sheets-Sheet 2

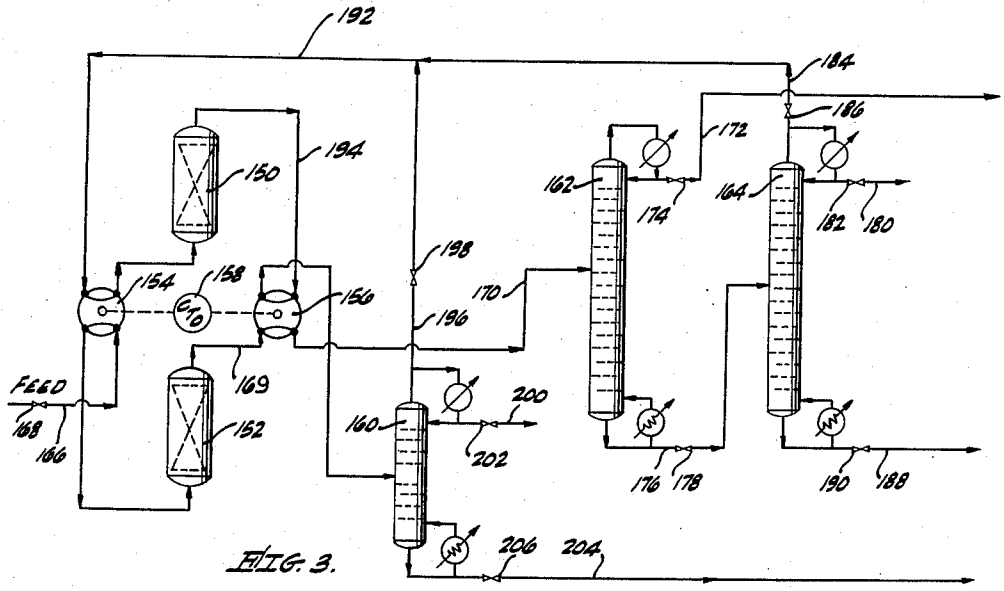


FIG. 3.

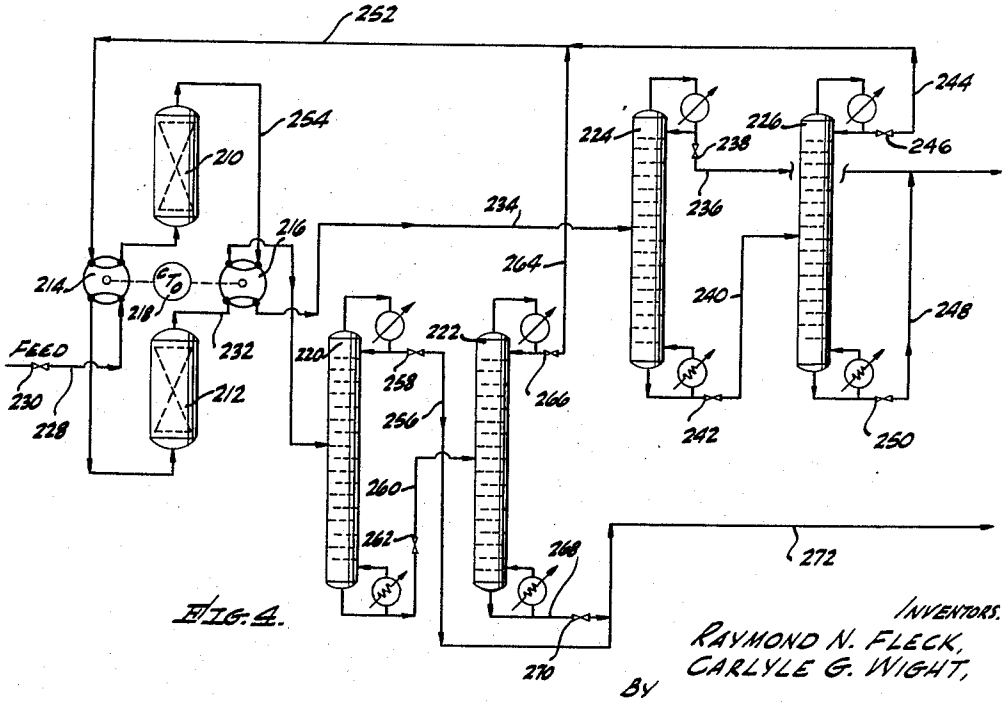


FIG. 4.

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FRACTIONATION PROCESS

Filed July 13, 1956 3 Sheets-Sheet 3

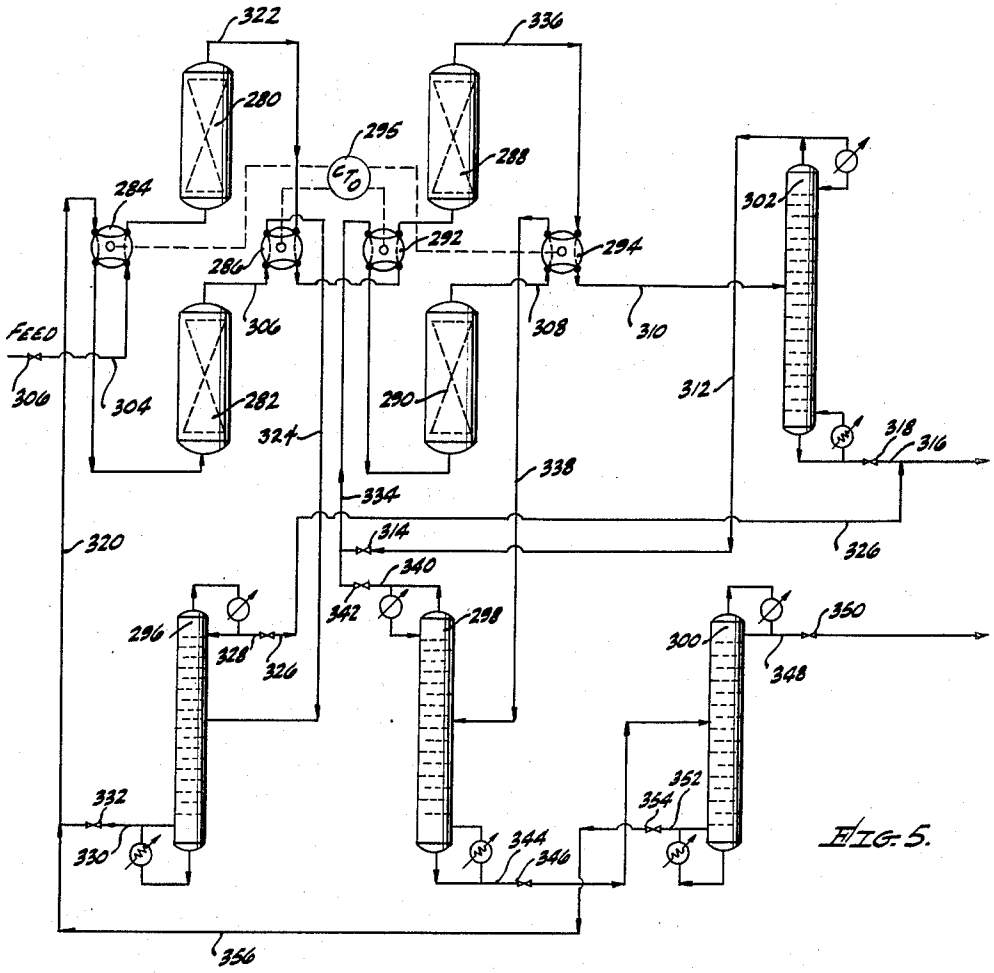
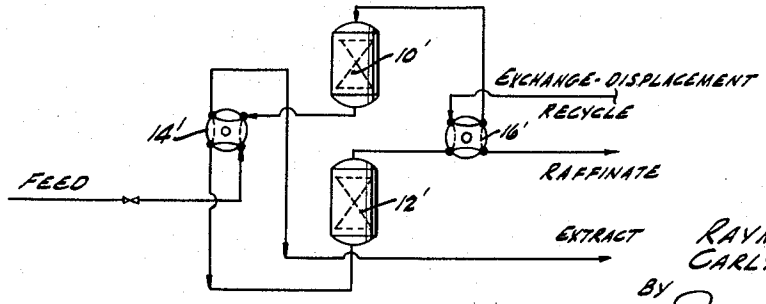


FIG. 5.

FIG. 6



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FRACTIONATION PROCESS

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Application July 13, 1956, Serial No. 597,742

7 Claims. (Cl. 208—310)

This invention relates to the fractionation of fluid mixtures, either gaseous or liquid, such as mixtures of hydrocarbons. The invention relates particularly to an improved process for the fractionation of complex hydrocarbon mixtures in the gasoline boiling range to produce a high antiknock rating gasoline through the selective removal of low antiknock rating components.

Gasoline improvement to raise the antiknock rating is required to provide an adequate fuel for modern high compression internal combustion reciprocating piston engines. Gasoline in general comprises many individual components, including hydrocarbons having between about 4 and about 12 carbon atoms per molecule. In this range are found many straight and branched chain paraffin hydrocarbons, straight and branched chain olefin hydrocarbons in cracked gasolines, as well as many naphthene and aromatic hydrocarbons. The complexity of gasoline stocks is appreciated by the fact that there are some 660 possible paraffin isomers and over 3800 olefin hydrocarbon isomers in this range of from 4 to 12 carbon atoms per molecule. In addition there are a great many naphthene and aromatic hydrocarbons. Each component has its own tendency to knock in internal combustion engines and its molecular character strongly governs this tendency. In general the straight chain or normal paraffin hydrocarbons have the greatest tendency to knock and therefore have the lowest antiknock rating. The naphthene hydrocarbons having slightly higher antiknock rating, followed by the normal olefins, the iso-olefins, the iso-paraffins, and the aromatic hydrocarbons have the highest antiknock rating.

The gasoline is a mixture therefore that has an antiknock rating which is a function of its composition. Straight-run gasoline generally has a low rating due to its relatively high normal paraffin content and relatively low iso-paraffin and aromatic content. Cracked gasolines on the other hand have higher antiknock ratings due to the presence of normal and iso-olefin hydrocarbons. Distillation alone is not especially effective in removing only the low antiknock rating components since the rating is essentially determined by molecular structure rather than boiling point.

In the past, effective antiknock rating increase has been accomplished by the addition of materials to the gasoline such as antiknock agents like tetraethyl lead and hydrocarbon components of very high knock ratings such as high branched chain hydrocarbons like the alkylate of iso-butane and iso-butylene, or aromatic hydrocarbons, and the like. Antiknock rating increase is also obtainable by high temperature treatment such as thermal or catalytic cracking, dehydroaromatization or reforming, and the like. Such treatment effectively converts some of the low antiknock rating components into components having higher knock ratings.

The addition of antiknock agents or of hydrocarbons of unusually high antiknock rating is expensive since usually they must be purchased or synthesized for such use. Even the high temperature treatments to raise the

knock rating is only partly effective since the product from these processes still contains appreciable quantities of low antiknock rating materials. For example, a desulfurized naphtha having a knock rating of 51 (F–1 clear) is reformed to effect dehydrogenation of normal paraffins and cyclization to form aromatics over a platinum catalyst to produce a product having a knock rating of 96 (F–1 clear). Although this knock rating is satisfactory in some cases, the product still contains about 13% by volume of normal paraffins whose antiknock ratings were of the order of 20 or less.

The present invention is therefore directed to an improved process for increasing the antiknock rating of straight-run or cracked gasolines without high temperature treatment, and which is also applicable to the improvement of fairly high antiknock rating gasolines such as those produced in high temperature thermal or catalytic treatments. Specifically the process comprises the separation of low antiknock components from these materials so as to leave only the high antiknock rating materials. The process involves the selective adsorption of normal paraffins or normal olefins from the mixture of hydrocarbons on the basis of their straight chain molecular shape. The process however does not require the usual high temperature desorption of the rich adsorbent which is conventionally used in all other adsorptive fractionation processes. Thus the adsorbent saturated with low antiknock rating components need not be heated, or stripped with a stripping gas, or both, to render it reusable in the process. Rather, the adsorbent is subjected to a novel and simple treatment in which an active exchange or displacement of the low antiknock rate materials is effected by means of a selected recycle stream of adsorbable hydrocarbons. The process thus produces an unadsorbed or raffinate stream of gasoline containing the recycle component which can be separated from the non-adsorbed material by ordinary distillation, and a desorbed or extract gasoline stream including adsorbed low antiknock rating materials together with the recycle component, which is also readily separable therefrom by distillation.

It is therefore a primary object of this invention to provide an improved fractionation process using a specific adsorbent which is active in adsorbing materials on the basis of their molecular size or shape.

It is a further object of this invention to provide an improved selective adsorption and distillation process for the fractionation of complex mixtures and which is characterized by the absence of the usual high temperature adsorbent-desorption treatment.

It is a specific object of this invention to provide a fractionation process for the separation of complex mixtures using a specific adsorbent, which selectively adsorbs components having linear or straight chain molecules, and including a desorption step which involves an exchange displacement with a recycle stream containing a substantial proportion of components having linear or straight chain molecules and which are readily separable, by virtue of a substantially different boiling point or range, from the straight chain materials adsorbed from the complex mixture.

It is a more specific object of this invention to provide an improved continuous process for gasoline fractionation to remove low antiknock rating components therefrom by alternately contacting a substantially compact bed of solid granular adsorbent with the gasoline fraction to adsorb straight chain olefins and paraffins therefrom, then contacting the adsorbent with a recycle stream of hydrocarbons readily separable by distillation from the feed stream and consisting of other straight chain olefins or paraffins so as to displace the components adsorbed from the gasoline fraction and pre-saturate the adsorbent

with straight chain components from the recycle stream, and finally distilling both the unadsorbed raffinate fraction and the desorbed or displaced extract fraction from the adsorbent so as to separate the straight chain recycle materials therefrom leaving an unadsorbed gasoline fraction of high antiknock rating and an adsorbed gasoline fraction of very low antiknock rating.

Other objects of the present invention will become apparent to those skilled in the art as the description and illustration thereof proceed.

Briefly the present invention comprises an improved fractionation process involving a combination of selective adsorption on a granular solid adsorbent and distillation of the fluids being treated so as to effect an improved separation of complex mixtures of components on the basis of their molecular species. The present invention will be described in connection with fractionation of a mixture of a complex mixture of hydrocarbons of the gasoline boiling range. Such mixtures contain many different hydrocarbon components having from about 4 to about 12 carbon atoms per molecule and which components are of different molecular species. The feed mixture, herein considered to be gasoline for purposes of example, is first passed through contact with a compact bed of solid granular adsorbent to adsorb more readily adsorbable constituents leaving the less readily adsorbable constituents as an unadsorbed raffinate phase. Instead of heating the resultant rich adsorbent and contacting it with a stripping fluid as in conventional adsorptive fractionation processes, in the present invention this rich adsorbent containing the more readily adsorbable constituents of the feed is contacted with a recycle stream of hydrocarbons containing adsorbable components and selected to have a boiling point or boiling range sufficiently different from that of both the adsorbed and unadsorbed phases of the feed gasoline that it may readily be distilled from the unadsorbed as well as from the adsorbed fractions of the feed. An active exchange displacement occurs in which the adsorbable recycle stream is adsorbed in exchange with and displacing the feed components previously adsorbed. This removal of the more readily adsorbable constituents in the adsorbed phase from the adsorbent by contacting the rich adsorbent with a recycled exchange displacement stream produces an extract stream comprising a mixture of the desorbed more readily adsorbable constituents of the feedstock plus the constituents of the recycle stream and the adsorbent is left saturated with recycle stream components. The extract stream is then distilled to recover the desorbed fraction from the recycle components. The adsorbent is then contacted with further quantities of the feedstock in which the more readily adsorbable components exchange with and displace the recycle components present on the adsorbent and produce a raffinate stream containing the unadsorbed components of the feed gasoline plus the desorbed recycle components. This effluent raffinate stream is also distilled to separate the unadsorbed fraction from the recycle components.

The recycle stream employed in the process of this invention for exchange displacement of the adsorbed feedstock materials from the adsorbent may be a mixture of adsorbable components, or a single pure adsorbable component, naturally occurring in the feedstock. The recirculated material however must have a different boiling point or boiling range from the boiling point or boiling range of the feedstock so that it is readily and economically separable from both the adsorbed phase components and the unadsorbed phase components of the feedstock. In the process the raffinate stream of unadsorbed materials from the adsorption zone as well as the extract stream of displaced adsorbed materials, both contain the recycled displacement exchange materials. Each of these streams is separately distilled, the recycle components are recirculated in the process to effect exchange displacement from the rich adsorbent, and the unadsorbed gasoline hydrocarbons and the adsorbed gasoline hydrocarbons are produced as separate products of the process. The character and antiknock rating of the hydrocarbons in these two product streams are governed by the nature of the selective adsorbent used in the process. With the adsorbent more particularly described below, only normal or straight chain paraffins, and normal olefins if present, are adsorbable. Therefore the extract phase displaced from the adsorbent contains the relatively low anti-knock rating materials. The unadsorbed raffinate phase contains the branched chain and naphthene and aromatic hydrocarbons whose molecular size renders them unadsorbable.

The adsorbent employed in the process of this invention is a solid granular material having a mesh size range between about 2 and 100 mesh and preferably between about 4 and about 30 mesh. It is used in the form of a dense compact bed of material through which the feed and displacement and exchange recycle streams pass, either in the vapor phase or in the liquid phase. The process may employ the adsorbent in the form of a single static bed of material in which case the process is only semicontinuous. Preferably a plurality of two or more static beds of adsorbent are employed with appropriate remotely operable valving so that the feed stream is passed through one or more of the adsorbers in a set while the exchange displacement stream passes through one or more of the other adsorbers in the set. In this case the feed and product flows are continuous, in either the vapor or liquid phase, and either up or down through the adsorbent. When the granular adsorbent is sufficiently rugged physically then the moving solids bed modification may be employed in which flow of feed is maintained continuously through an adsorption zone, the flow of displacement exchange fluid is maintained continuously through a desorption zone, and the granular adsorbent is recirculated successively through these two zones. With the smaller sized mesh ranges of adsorbent, the material may be fluidized in and by the fluid streams contacting it, although the compact bed modifications are preferred since a greater number of theoretical and actual contact stages are more readily obtained in smaller and simpler equipment.

The adsorbents employed in practicing the present invention are the natural or synthetic zeolitic crystalline partially dehydrated metallo alumino silicates. The composition of one typical synthetic zeolite having a pore size of about 4 A. is $[Na_2O \cdot Al_2O_3 \cdot (SiO_2) \cdot_2]$. It may be prepared by heating stoichiometric quantities of alumina and silica and excess caustic under pressure. The excess is washed out and the desired metal ion may then be introduced by ion exchange. Part of the sodium in this material can be ion exchanged with concentrated salt solutions at superatmospheric pressure and temperatures of 150–300° C. to introduce other metal ions such as calcium to produce

$$[CaO \cdot Al_2O_3 \cdot (SiO_2)_2]_{0.7}[Na_2O \cdot Al_2O_3 \cdot (SiO_2)_2]_{0.3}$$

having a pore size of about 5 A. Certain naturally occurring minerals, such as chabazite, analcite, gmelinite, and the like, can be heated to dehydrate the molecule and obtain an activated zeolitic adsorbent similar in adsorption properties to the manufactured materials. These natural and synthetic materials are all zeolites and their sodium and calcium derivatives are very stable adsorbents which apparently have "pores" available for adsorption which are quite uniform in size. Other derivatives have different sized "pores." The molecules which are the more readily adsorbable and for which the adsorbent exerts preferential adsorptive forces are those having straight chain molecules whose minimum dimensions are equal to or slightly less than these pore dimensions. Thus the normal paraffins and normal olefins with cross chain dimensions of under 5 A. are very strongly and very readily adsorbed by these materials. However the branched

chain paraffins or olefins, and the naphthene and aromatic hydrocarbons, all having molecular dimensions in the shortest direction in excess of 5 A. are substantially non-adsorbable. These adsorbents are thus selective for normal paraffins, and normal olefins if present, and will not adsorb any appreciable quantity of other hydrocarbons. Other derivatives of these particular inorganic adsorbent materials have uniformly sized pores as high as from 12 to 13 A. and these will adsorb molecules having a dimension less than about 12 A. and will exclude a material whose minimum molecular dimension is above 12 A.

The synthetic crystalline partially dehydrated metallo alumino silicate zeolitic adsorbents are presently available items of commerce marketed by Linde Air Products Company, 30 E. 42nd Street, New York 17, New York, under the name of "Molecular Sieves 4A, 5A, 13X, etc."

The present metallo alumino silicates adsorb polar molecules to a certain extent. In gasoline treating this interferes with the fractionation of gasoline hydrocarbons as a function of molecular shape. Accordingly it is contemplated in this invention to contact the feed stream first with a material which exhibits very strong adsorptive forces for these polar materials and remove them from the stream to be treated. This pre-adsorption or pre-treating of the feed may be accomplished by contacting the feed stream with an inorganic halide such as copper chloride, calcium chloride, magnesium chloride, and the like. In this way large and highly polar materials such as ethers, thioethers, water, alcohols, mercaptans, and amines are readily removed from the feed. Also removable in this way are the highly polar nitrogen and sulfur compounds which commonly occur in small amounts in gasolines. These specifically include such materials as thiophene and the alkylated thiophenes, pyridine and alkylated pyridines. Thus this pre-treatment removes these polar materials and prevents them from interfering with the subsequent fractionation in which the feed is separated into streams containing components of a specific molecular size or structure.

Although the pre-adsorption step prevents rapid deactivation of the main adsorbent beds, some deactivation may eventually occur. It is within the contemplation of this invention to regenerate the adsorbent by high temperature stripping with steam etc. to desorb impurities, with hot flue gas, to burn off the impurities as in catalyst regeneration, or both.

The process of this invention and the modifications thereof, as well as several forms of apparatus employed to carry out the process, will be more readily understood by reference to the accompanying drawings, each of which is described in connection with its application to the fractionation of gasoline as a specific example and in which:

Figure 1 shows a schematic flow diagram of a simple modification of the process of this invention adapted to contact continuously a feed gasoline stream with two fixed beds of adsorbent and utilizes either a liquid or vapor phase feed contact with a relatively low boiling displacement exchange recycle stream,

Figure 2 shows a modification of the process of Figure 1 adapted to the use of a recirculating or moving adsorbent stream,

Figure 3 shows a third modification of the present process in which the recirculated displacement exchange stream is of an intermediate boiling range or boiling point with respect to the unadsorbed stream and which is therefore heart cut from the unadsorbed or raffinate portion of the feed,

Figure 4 shows another modification of this invention in which the displacement exchange stream is of an intermediate boiling point or boiling range with respect to both the adsorbed and unadsorbed streams and is thus heart cut from both of these streams for recycle,

Figure 5 shows still another modification of this invention which is applied to the successive contact of the feedstock in two or more adsorbent stages, for example to adsorb normal olefins from the feed in the first stage to recover them for blending into a high knock rating gasoline and adsorbs normal paraffins in the second stage to reject them as a low antiknock rating product stream, and

Figure 6 shows an alternate control valve connection which causes the feed and the exchange-displacement streams to flow in opposite directions through the adsorbent beds.

Example I

Referring now more particularly to Figure 1, the simplest modification of the present invention is shown in the form of a schematic flow diagram. Two adsorbers **10** and **12** packed with a compact mass of granular metallo alumino silicates having pore openings approximating 5 A. are shown. Adsorbers **10** and **12** are used in alternation with each other and the appropriate flow changes are effected by means of four-way control valves **14** and **16** actuated by cycle timer **18**. In the position shown adsorber **10** is being desorbed while adsorber **12** is contacting fresh feed. Vessel **20** is provided as a pre-adsorber or guard chamber to remove highly polar materials from the feedstock.

A depentanized gasoline is passed in the vapor phase through line **22** at a rate controlled by valve **24** through pre-adsorber **20** wherein polar materials are removed from the feed. This pre-treated feed continues through line **26** through the interconnected ports in valve **14** and then through line **28** through adsorber **12**. Herein an active displacement exchange takes place between the normal paraffins in the gasoline stream and normal butane which is employed in this modification for the recycle stream and which saturates the adsorbent prior to contact with the feed. The normal butane recycle stream in this invention is substantially lower in boiling point than any component of the feed. The normal butane pre-saturating the adsorbent is exchanged with the normal paraffins of the feed stream so that the adsorbent in adsorber **12** finally becomes substantially saturated with these heavier normal paraffins. The effluent or raffinate stream from adsorber **12**, containing the non-adsorbable gasoline components together with the exchanged normal butane, passes on through line **30** through the interconnected ports in valve **16** and through line **32** into raffinate fractionator **34**. This distillation column is provided with an overhead condenser **36** and reboiler **38**. The raffinate is distilled separating the normal butane from the normal paraffin-free gasoline. The normal butane recovered from the gasoline is passed in the vapor phase through line **40** at a rate controlled by valve **42** into displacement exchange recycle line **44**. The treated gasoline is removed from the bottom of the column and is passed to further processing or storage facilities not shown through line **46** at a rate controlled by valve **48**. Because of the elimination of normal paraffins from this gasoline stream, the antiknock rating is readily increased by 7 to 10 points.

The normal butane exchange displacement recycle stream flows on through line **44**, through the interconnected ports of four-way control valve **14**, and then through line **50** to adsorber **10** which is now in the desorption part of the cycle. The normal butane passes in the vapor phase through the adsorbent saturated with normal paraffins from the previous feed contacting step. A reverse displacement exchange takes place whereby the normal paraffins from the gasoline are displaced from the adsorbent and it adsorbs normal butane instead. Flowing from the top of adsorber **10** through line **52** is a desorbed extract stream comprising a rich mixture of normal paraffins desorbed from the adsorbent and normal butane used in their desorption. This stream passes through the interconnected ports of valve **16** on through line **54** into extract distillation column **56**, provided with overhead condenser **58** and reboiler **60**. The normal butane present in the extract stream is distilled from the normal paraffins removed from the gasoline feed. The

normal butane flows through line 60 in the vapor phase at a rate controlled by valve 62 and is returned to and through displacement exchange recycle manifold 44. The very low antiknock extract, comprising a concentrated mixture of normal paraffins, is removed from the system through line 64 at a rate controlled by valve 66. Thus the high antiknock fraction is produced from the process through line 46 containing substantially no normal paraffins, while the low antiknock gasoline fraction is produced through line 64 containing substantially all of the normal paraffins of the feed.

In the event that the feed stream contains normal butane, the net product of normal butane from the system over and above that required from the displacement exchange recycle may be removed through column 34 via line 68 at a rate controlled by valve 70, or it may be removed through column 56 through line 72 at a rate controlled by valve 74.

In the foregoing example it should be noted that the displacement exchange recycle stream consisted of normal butane vapor which is lighter or has a lower boiling point than any of the components present in the feed stream. It should also be noted that both the adsorption and desorption steps of the process are conducted in the vapor phase.

Example II

In the present invention it has been found that olefin hydrocarbons of the straight chain type are more strongly adsorbed than are normal paraffins having the same number of carbon atoms as the olefin. It has been determined that the metallo alumino silicate adsorbents appear to have about an equal preference for a straight chain olefin and for a straight chain paraffin having three more carbon atoms per molecule than the olefin. This discovery is utilized according to the present invention by modification of the process described in connection with Figure 1 so as to employ low molecular weight olefin as the exchange displacement recycle and which has about three carbon atoms per molecule less than the mol average of the more readily adsorbable paraffins. In this case gaseous ethylene is used as the olefin and is found to displace very effectively from the adsorbent the normal paraffins adsorbed from the gasoline. In Figure 1 the feed stream flows as before through adsorber 12 into fractionator 34. In adsorber 12 the gasoline normal paraffins are adsorbed on the adsorbent displacing ethylene therefrom, and in column 34 the gaseous ethylene is stripped from the nonadsorbed raffinate gasoline and recirculated through line 44. The gaseous ethylene flows from line 44 through adsorber 10 into extract still 56. The gaseous ethylene in adsorber 10 exchanges with the gasoline normal paraffins on the adsorbent and extract still 56 strips the gaseous ethylene for recirculation from these gasoline normal paraffins. It is found that the olenfin in this case is somewhat more effective in displacing gasoline normal paraffins from the adsorbent than was the normal butene.

Example III

The process shown in Figure 1 is also readily applicable to the treatment of relatively narrow boiling range feed streams using as a displacement exchange recycle stream a component which has an intermediate separation factor between the two fractions which it is desired to separate from the feed. For example, in the process shown in Figure 1 a C_6 cut of cracked (olefinic) gasoline is passed in the vapor phase through adsorber 12 in contact with the adsorbent which is already saturated with normal octane as the displacement exchange component. The normal octane is of an intermediate adsorbability between the normal hexene for which the adsorbent exerts strong adsorptive forces, and normal hexane for which the adsorbent exhibits weaker adsorptive forces. The raffinate from adsorber 12 consists of the normal octane recycle components and the nonadsorbed raffinate components, in this case comprising normal hexane. In raffinate still 34 the normal hexane is produced from the top of the still through line 68 at a rate controlled by valve 70 while the recycle component normal octane accumulates at the bottom of column 34 and is recirculated in the vapor phase through line 76 controlled by valve 78 wherefrom it passes through line 80 into recycle manifold 44. The normal octane flows through adsorber 10 which is in the desorption part of the cycle and here it exchanges with the normal hexene to produce an extract stream through line 52 comprising normal octane and normal hexene. This extract flows to fractionator 56 in which the normal hexene is produced as an overhead product through line 72. It has a relatively high knock rating and may, if desired, be combined with other high antiknock rating components to produce a quality gasoline. The normal octane recycle component is removed from the bottom of still 56 through line 79 and is controlled by valve 82 and passes through line 84 back into recycle manifold 44 for recirculation in the system.

In this modification it is noted that the displacement exchange component is of intermediate adsorbability between normal hexene and normal hexane but it is of a higher boiling point so that it is produced for recycle as a bottoms product in both the extract and raffinate stills.

Example IV

The process shown in Figure 1 was also applied to the vapor phase removal of normal paraffins from a depentanized light gasoline which had been reformed over a platinum catalyst. Normal pentane was employed as the displacement exchange recycle stream. The feed had a knock rating (motor method, clear) of 66.8. Using a bed of metallo alumino silicate adsorbent having 5 A. pores the raffinate or unadsorbed treated gasoline had a knock rating of 78.4 while the adsorbed normal paraffin or extract stream had a knock rating 17.2. The leaded knock rating of the treated gasoline raffinate (research method+3 ml. TEL) was 97.9. The normal paraffin recycle adequately displaced and exchanged with the gasoline normal paraffins from the adsorbent so that continued treatment of the feed gasoline was permitted.

Example V

The treating of reformed depentanized gasoline, discussed immediately above, was continued through 30 cycles, contacting the feed gasoline to adsorb normal paraffins in alternation with a displacement exchange step with normal pentane vapors to regenerate. Over this period no decrease in the quantity adsorbed or the ability of the adsorbent to remove normal paraffins from the feedstock was noted. In one run an F–2 clear octane rating of the adsorbed material of as low as 9.8 was noted and simultaneously the raffinate knock rating (F–1 clear) was 83.7. The leaded knock ratings of the unadsorbed phase in each of the 30 cycles all fell between 97.5 and 98.3.

Example VI

The process shown in Figure 1 was applied to the treating of light alkylate having a clear research octane rating of 96.4. This material contains highly branched hydrocarbons and substantially no straight chain hydrocarbons. The volume of the feed which was adsorbed on the adsorbent was substantially zero at 280° F. and the unadsorbed raffinate product had the same knock rating of 96.4.

Example VII

The process of Figure 1 was applied to the removal of normal paraffins from a catalytically hydrocracked gasoline boiling between 120° F. and 402° F. The feed had a research octane rating with 3 ml. TEL of 94.9. At an adsorption temperature of 403° F., approximately 6 volume percent of the feed was adsorbed and the unadsorbed raffinate gasoline had a research octane rating with 3 ml. TEL of 97.3.

Example VIII

The process of Figure 1 was applied to the removal of normal paraffins from hydrogenated shale oil coker distillate gasoline boiling between 120° F. and 400° F. At an adsorption temperature of 403° F., approximately 25% by volume of the feed was adsorbed and the unadsorbed gasoline raffinate had a research octane rating+3 ml. TEL of 88.3 average. The knock rating of the feedstock was 76.0.

Example IX

In a pair of identical 30 cycle tests on platinum-reformed light gasoline, the process of Figure 1 was first employed using normal pentane as the exchange displacement recycle stream. In the first case a depentanized platinum reformed gasoline having a research octane rating of 3 ml. TEL of 89.8 was treated to produce an unadsorbed gasoline raffinate having an average knock rating of 96.2. This is an average increase of 6.4 octane numbers.

In the second case, a dehexanized platinum reformed light gasoline, having a research octane rating of 91.0 (with 3 ml. TEL), was treated under identical conditions to produce an unadsorbed gasoline raffinate product having an average knock rating of 97.9 for an average increase of 6.9 octane numbers.

Example X

In the process of this invention employing the metallo alumino silicates as adsorbents, it is found that in the liquid phase the adsorbent has a tendency to adsorb the lower molecular weight normal paraffins in preference to the higher molecular weight normal paraffins. This is just the reverse of the tendency for adsorption in the vapor phase. Applying this in the process of Figure 1, a C_6 to C_{10} gasoline was treated using normal butane in the liquid phase as the desorption exchange recycle. In this case the feed passes through line **22** into and through adsorber **12** wherein the normal paraffins in the C_6 to C_{10} range are adsorbed and exchanged for normal butane in the vapor phase. The nonadsorbed high knock rating gasoline is fractionated in raffinate still **34** producing a bottoms product of high antiknock rating gasoline and the normal butane is produced as an overhead product. In this modification the normal butane is produced in the liquid phase through line **86** controlled by valve **88** and passed into and through recycle manifold **44** to adsorber **10** which is in the desorption part of the cycle. Adsorber **10** is contacted with liquid normal butane and it displaces and exchanges with the adsorbed C_6 to C_{10} normal paraffins adsorbed from the gasoline during the previous cycle. The extract stream flows through lines **52** and **54** into extract still **56**. Here the displaced low antiknock rating normal paraffins are produced from the bottom of the column, the recycled normal butane in the liquid phase is removed from the top of the column through line **90** controlled by valve **92**, and is returned through manifold **44** to contact further quantities of rich adsorbent.

In the foregoing example, because of the change in phase between adsorption and desorption and because of the reversal of the preference of adsorption, both the adsorption and desorption steps are substantially 100% efficient.

Referring now more particularly to Figure 2 a modification of the process shown in Figure 1 is described in which a recirculating stream of adsorbent is employed. The inlet and outlet cycle valves have been eliminated. In this figure the essential elements of the present invention include adsorption zone **100**, desorption zone **102**, solids conveyor **104**, raffinate still **106**, and extract still **108**. Feed gasoline is passed through line **110** at a rate controlled by valve **112** through adsorption zone **100** in which the normal paraffins and other straight chain hydrocarbons are adsorbed thereby displacing and exchanging with the recycle components saturating the adsorbent. The raffinate passes through line **114** to raffinate still **106**. Reboiler **116** and overhead condenser **118** are provided. The unadsorbed raffinate gasoline having a high antiknock rating is produced through line **120** controlled by valve **122** as a product of the process. The exchange displacement recycle stream separated from the raffinate passes in the vapor phase through line **124** into recycle manifold **126** and is introduced into desorption zone **102**. Herein the recycle stream exchanges with and displaces the adsorbed normal paraffins from the feed producing an extract which flows through line **128** into extract still **108**. Reboiler **130** and overhead condenser **132** are provided. Herein the extract is separated into a low antiknock rating gasoline, consisting essentially of normal paraffins, which is produced as a product through line **134** controlled by valve **136**. The displacement exchange components separated from the extract pass through line **138** controlled by valve **140** into recycle manifold **126**. Any components occurring in the feed which are the same as those used for the exchange displacement cycle can be accumulated as an excess in the system and can be produced therefrom as products from either or both of raffinate still **106** or extract still **108** through lines **142** and **144** respectively.

In this modification the adsorbent passes downwardly by gravity as a substantially compact moving bed through adsorber **100** exchanging its adsorbed recycle components for the adsorbable straight chain components of the feed. The rich adsorbent is then conveyed through conveyor **104** and introduced into desorption zone **102**. Here it passes downwardly as a moving bed in contact with the displacement exchange recycle stream. In contact therewith it gives up its adsorbed straight chain gasoline hydrocarbons and adsorbs components of the recycle stream thus producing a regenerated adsorbent and the extract. The regenerated adsorbent is introduced through line **146** into the top of adsorption zone **100** for repassage therethrough.

In the process of Figure 2 utilizing a moving bed of granular contact material, it is within the contemplation of this invention to employ any or all of the well known steps and apparatus elements characteristically employed with moving bed processes. Since these are well known they have not been detailed but are well understood by those skilled in the art. It is also contemplated to use the same feed pre-treating steps described in connection with Figure 1 in the processes described in conjunction with Figures 2 through 6.

Referring now more particularly to Figure 3, a schematic flow diagram of this invention is shown modified so as to employ a component of the feed stream as the recirculated exchange displacement component for desorbing the adsorbed materials from the feed.

Example XI

In Figure 3 the essential elements of the process include adsorbers **150** and **152**, control valves **154** and **156**, cycle timer operator **158**, extract still **160**, and raffinate heart cutting stills **162** and **164**. The adsorbent used is the metallo alumino silicate having pores of approximately 5 A. size. A light fraction of gasoline, reformed on a platinum catalyst, contains in addition to the aromatic hydrocarbons having high antiknock ratings, the iso and normal hexanes, heptanes, octanes, and nonanes with relatively low antiknock ratings. The feed introduced through line **166** controlled by valve **168** through the interconnected ports of valve **154** through first adsorber **152** in which the adsorbent is saturated with normal hexane. The raffinate consisting of aromatic hydrocarbons in this boiling range and the branched chain isomers of hexane, heptane, octane, and nonane together with the displaced and normal hexane flows through line **169** through the interconnected ports of control valve **156** through line **170** to the first heart cutting column **162**. The raffinate heart cutting stills are provided with over-

head condensers and bottoms reboilers as in previous examples. The overhead product from still **162** is produced through line **172** controlled by valve **174** and consists of iso-hexane and any lower boiling components. The bottoms product from the first still contains the displaced normal hexane together with the unadsorbed branched chain hydrocarbons in the C_6 through C_9 range and unadsorbed aromatic hydrocarbons in this same boiling range. This material flows through line **176** controlled by valve **178** into second heart cutting still **164**. The lightest material in this stream is the displacement exchange recycle stream of normal hexane. The net product of normal hexane is removed from the top of the column through line **180** controlled by valve **182** and the remainder is removed as an overhead vapor product through line **184** controlled by valve **186** as part of the exchange displacement recycle stream. The bottoms product is removed from still **164** through line **188** at a rate controlled by valve **190** and consists of the unadsorbed aromatic hydrocarbons and branched chain hydrocarbons boiling in the C_6 to C_9 range. This material together with the iso-hexane produced through line **172** may be combined if desired to produce high antiknock rating fuel substantially freed of normal paraffins.

The normal hexane recycle stream flows through recycle manifold **192**, through the interconnected ports of valve **154** into and through adsorber **150** which is in the desorption or displacement exchange part of the cycle. Herein the normal paraffins in the C_6 through C_9 range adsorbed on the adsorbent are exchanged for and displaced by the normal hexane in the recycle stream. The extract stream consisting essentially of normal paraffins flows through line **194** and through the interconnected ports of control valve **156** to extract still **160**. This still is also provided with an overhead condenser and bottoms reboiler. Herein the normal hexane, sufficient to make up the required amount of displacement exchange recycle, is removed in the vapor phase through line **196** controlled by valve **198** and combined with the overhead vapor from second heart cutting still **164** in recycle manifold **192**. A net product of normal hexane may be produced, if desired, through line **200** controlled by valve **202** from the top of still **160**. The adsorbed normal paraffins in the C_6 through C_9 range are removed from the bottom of extract still **160** through line **204** at a rate controlled by valve **206** and sent to further processing or storage facilities not shown. This concentrate consists of a very low antiknock rating gasoline stream.

Referring now particularly to Figure 4, the schematic flow diagram of another modification of the process of this invention is shown in which the exchange displacement recycle stream is a straight chain component which has a boiling range intermediate both the unadsorbed raffinate components and the adsorbed extract components of a wide range feedstock. The essential elements of the modification of Figure 4 include adsorbers **210** and **212** containing metallo alumino silicate adsorbents having 5 A. pores, four-way control valves **214** and **216** operated by cycle timer **218**, the extract heart cutting stills **220** and **222**, and the raffinate heart cutting stills **224** and **226**.

Example XII

In the process of Figure 4 a gasoline fraction containing normal and branched chain hydrocarbons of from 6 to 10 carbon atoms per molecule, and which may contain also naphthene and aromatic hydrocarbons of this boiling range, is introduced through line **228** controlled by valve **230**, through control valve **214** and into adsorber **212** wherein the straight chain normal paraffins are adsorbed and exchanged with normal octane which is the exchange displacement recycle component in this modification. The unadsorbed hydrocarbons including the branched chain paraffins and other non-adsorbed hydrocarbons together with the displaced normal octane flows through line **232** through valve **216** through line **234** into first column **224** of the raffinate heart cutting stills. Each of the heart cutting stills is provided with an overhead condenser and a bottoms reboiler as in previous modifications. The overhead product from first raffinate heart cutting still **224** is removed through line **236** controlled by valve **238** and consists of the unadsorbed branched chain hydrocarbons in the C_6 through C_8 range together with traces of the branched chain C_9 hydrocarbons. This is a high antiknock rating stream. The bottoms fraction from first raffinate heart cutting still **224** is introduced through line **240** controlled by valve **242** into second raffinate heart cutting still **226**. This stream consists of the displaced normal octane together with the remaining unadsorbed branched chain hydrocarbons of the C_9 and C_{10} species. In the second still **226** the overhead vapor is recirculated through line **244** controlled by valve **246** and consists essentially of the exchange displacement stream of normal octane together with a trace of iso-nonanes. The bottoms product from second still **226** is a high antiknock gas stream consisting of branched chain hydrocarbons of 9 and 10 carbon atoms per molecule. This stream may be produced separately or it may be passed through line **248** controlled by valve **250** with the lower boiling branched chain hydrocarbons flowing through line **236**. This stream is the raffinate and contains the high antiknock components of the feed.

The normal octane exchange displacement recycle is returned through line **252** through valve **214** into and through adsorber **210** which is in the desorption part of the cycle. Herein it exchanges with and displaces the adsorbed straight chain paraffins previously adsorbed from the feed and producing extract consisting of the desorbed C_6 through C_{10} normal paraffins and part of the recirculated normal octane. This extract flows through line **254** and valve **216** through first extract heart cutting still **220**. The overhead product from the still consists of normal hexane and normal heptane and is removed through line **256** controlled by valve **258**. The bottoms product consisting of normal octane, nonane, and decane passes through line **260** controlled by valve **262** into second extract heart cutting still **222**. Herein the recirculated normal octane displacement exchange stream is removed as an overhead product through line **264** controlled by valve **266** and combined with the overhead product from the second effluent heart cutting still **226** for recirculation to the adsorbent being desorbed. The bottoms fraction of still **222**, flowing through line **268** controlled by valve **270** contains the normal straight chain paraffins having 9 and 10 carbon atoms per molecule and which may be combined with the lighter normal paraffins produced overhead from still **220** to produce a low antiknock rating gasoline through line **272**. It should be noted in the present case that the normal octane recycle employed in this modification is in the liquid phase while the feed to the adsorbers is passed in the vapor phase. Because of the intermediate adsorption preference for the normal octane, it is recovered from the extract and from the raffinate by a double heart cutting distillation.

Referring now to Figure 5, a still further modification of the process of this invention is shown which is especially adapted to the treatment of cracked gasoline streams containing both normal and branched chain paraffin and olefin hydrocarbons. The esential elements of this modification include olefin adsorbers **280** and **282**, with associated four-way control valves **284** and **286**, paraffin adsorbers **288** and **290** with associated control valves **292** and **294**, olefin extract still **296**, paraffin extract stills **298** and **300**, and raffinate still **302**. All of these stills are provided as before with overhead condensers and bottoms reboilers. The adsorbers contain metallo alumino silicate adsorbent having approximately 5 A. pores. It is found that because of the polar nature of normal olefin hydrocarbons they are considerably more strongly adsorbed

than normal paraffins having the same number of carbon atoms. Therefore in this modification the feed stream is contacted twice in succession with the adsorbent, first to adsorb normal olefins from the feed and second to adsorb normal paraffins from the first adsorber raffinate to produce a product raffinate of a high antiknock rating. This modification also permits the separate recovery and reuse of the normal olefins which have relative high antiknock rating and rejection of normal paraffins which do not.

Example XIII

A cracked gasoline feedstock and containing normal and branched chain paraffins and olefins having from 6 to 9 carbon atoms per molecule boiling below about 425° F. is passed in the vapor phase through line **304** controlled by valve **306** through control valve **284** to olefin adsorber **282** previously saturated with a first displacement exchange recycle stream consisting of normal paraffins in the C_{10} and C_{11} range, i.e. those which boil in or above the upper gasoline boiling range. The normal olefins are adsorbed herein and produce a first raffinate consisting of the unadsorbed branched chain paraffins as well as the unadsorbed branched chain and normal olefins together with the displaced higher normal paraffins of the first displacement exchange recycle stream. This first raffinate flows through line **306** and control valves **286** and **292** into paraffin adsorber **290**. Here the higher normal paraffins of the first displacement exchange recycle stream together with the normal paraffins of the feedstock are adsorbed and displace a relatively low molecular weight olefin hydrocarbon, in this case normal pentene, or other olefin boiling near the lower end of the gasoline boiling range, e.g. on the order of 50–100° F. The second raffinate produced from adsorber **290** consists of the unadsorbed branched chain paraffins and olefins of the feedstock together with the normal pentene which is the second exchange displacement component. This material flows through line **308** and valve **294** and through line **310** into raffinate still **302**. The overhead product from raffinate still **302** consists of substantially pure normal pentene which is the second exchange displacement recycle stream. This material is recirculated through line **312** controlled by valve **314** and is recirculated together with the normal pentene overhead vapor from paraffin extract still **298**, hereinafter described. The bottoms product from raffinate still **302** is produced through line **316** controlled by valve **318** and consists of the unadsorbed iso-olefins and iso-paraffins of the feedstock having between 6 and 9 carbon atoms per molecule. This is a high antiknock rating gasoline stream.

The first recycle stream employed to exchange with and displace the adsorbed normal olefins is a relatively heavy normal paraffin mixture of C_{10} and C_{11} hydrocarbons. This material is recirculated through line **320** through valve **284** and through olefin adsorber **280** which is in the desorption part of the cycle. Here the first recycle stream paraffins are adsorbed and displace the adsorbed normal olefins from the adsorbent. The olefin extract consisting of normal olefins in the C_6 through C_9 range together with the first recycle C_{10} and C_{11} normal paraffins flows from adsorber **280** through line **322**, valve **286**, line **324** into olefin extract still **396**. The adsorbed normal olefins are produced therefrom as an overhead product through line **326** controlled by valve **328** and may be blended with the high antiknock rating unadsorbed components of the feed flowing through line **316** from the bottom of raffinate still **302**. The normal olefin-free first recycle stream is removed from the bottom of olefin extract still **296** through line **330** controlled by valve **332** and is recirculated through line **320** to displace additional normal olefins from the adsorbent.

In the second adsorption stage, the desorption of adsorbed normal paraffins is accomplished by means of the second recycle stream consisting of normal pentene. This stream passes through line **334**, valve **292**, into and through paraffin adsorber **288** which is being desorbed. The paraffin extract is produced therefrom through line **336** and consists of normal pentene of the second recycle stream together with desorbed normal paraffins in the C_6 through C_9 range. This paraffin extract flows through valve **294** and line **338** into paraffin extract still **298**. The second recycle stream being of lower boiling point is produced as an overhead product through line **340** controlled by valve **342**. This normal pentene is combined with that separated from the raffinate in raffinate still **302** and the combined stream is recirculated as the second recycle stream in the process.

The desorbed normal paraffins in the C_6 through C_9 range together with traces of the C_{10} and C_{11} heavy paraffin of the first recycle stream are produced as a bottoms product from paraffin extract still **298** through line **344** controlled by valve **346** and are introduced to second paraffin extract still **300**. The overhead product from this still consists of the desorbed normal paraffins originating in the feed stream, namely the C_6 through C_9 paraffin hydrocarbons, and they are produced as a low antiknock rating gasoline product through line **348** controlled by valve **350**. Because the paraffin extract was derived in adsorber **288** from an adsorbent previously contacted with the olefin raffinate from adsorber **280**, which in turn had been previously desorbed by the first recycle stream consisting of heavy paraffins, the desorbed normal paraffins of the feed are contaminated with small amounts of the C_{10} and C_{11} normal paraffins of the first recycle stream. These materials are separated as a bottoms product from still **300**, are recirculated through line **352** controlled by valve **354** and pass through line **356** into admixture with the heavy paraffins of the first recycle stream produced as a bottoms product from olefin extract still **296**. This heavy paraffin mixture provides the first recycle stream employed to exchange with and displace the adsorbed normal olefins.

In the modification of the process one or more normal paraffins having a boiling point above the end point of the feedstock is employed as the first recycle stream to exchange with and displace the normal olefins first adsorbed from the feedstock and from which such heavy paraffins are readily separable by distillation. The second recycle stream in the modification comprises a normal olefin having a normal boiling point below that of the lightest component of the feed stream and which, because of its greater adsorbability, can successfully be desorbed and displace higher molecular weight normal paraffins. It is also readily separable by distillation from the desorbed normal paraffins of the feedstock.

In Figure 6, the schematic flow diagram of Figure 1 has been modified so that valves **14'** and **16'** route the feed up through the adsorbent beds in adsorbers **10'** and **12'** and the exchange-displacement recycle down through it. The reverse type of opposed flow can of course be used if desired by appropriate reconnection of the valves. Such opposed flow of feed and recycle streams can be used in any of the processes described and illustrated above, and has been found to be a highly efficient contacting method.

The foregoing description of several modifications of the present invention will serve to explain to those skilled in the art the principles of the present invention and the application thereof to various complex mixtures. Although the examples herein given have been directed to the fractionation of complex mitxures of hydrocarbons, this is not to be understood as a limitation of the process of this invention since the same principles may readily be applied to other mixtures of materials. Furthermore, the adsorbent materials specified in the foregoing examples have been specified as the metallo alumino silicate presently available. This also is not intended to be a limitation since other adsorbents can be substituted depending on the nature of the feed stream and the adsorp-

tion characteristics on the materials to be adsorbed therefrom. These particular inorganic adsorbents with their uniform pore sizes have been specified here since they are preferred in the illustrative applications of the process of this invention to the removal of straight chain paraffins and olefins from gasoline streams. These hydrocarbons are usually present in a minor proportion, particularly with reformed gasolines, so that the unadsorbed materials consist of aromatic and branched chain paraffin hydrocarbons of high antiknock rating.

The process of this invention thus consists of an improved fractionation process for complex mixtures employing the principles of solid adsorption and distillation in such a way so as to remove specific materials from the feed stream by means of the adsorbent and whereby the ordinary heating and gas stripping or liquid washing of the rich adsorbent have been completely eliminated. The process of this invention may be operated under pressure or under vacuum, and the actual operating pressures are actually determined by the pressure at which the feed stream is available and its boiling range, and whether the material being contacted is desirably in the vapor phase or the liquid phase. The proper operating pressure can be determined by those skilled in the art from known physical characteristics of the materials to be separated; namely the bubble point and dew point of complex hydrocarbon mixtures and the known way in which these change with pressure. The adsorption temperatures employed in the process of this invention are also determined by the physical characteristics of the feed stream and the operating pressure and also whether a vapor phase or a liquid phase contact is desired. In the complex gasoline streams the operating temperature is largely determined by the dew point and the bubble point of the stream at a given operating pressure. For example, adsorption temperatures above the dew point will obviously be in the vapor phase while operating temperatures below the bubble point will be in the liquid phase. It is within the contemplation of the present invention to adsorb to feed stream at a temperature between its bubble point and its dew point so that a mixed phase adsorption or displacement exchange desorption will be maintained for some special streams and obviously the feed contact may be in the vapor phase followed by recycle stream contact in the liquid phase, or vise versa, if desired.

A particular embodiment of the present invention has been hereinabove described in considerable detail by way of illustration. It should be understood that various other modifications and adaptations thereof may be made by those skilled in this particular art without departing from the spirit and scope of this invention as set forth in the appended claims.

We claim:

1. The process for treating a petroleum hydrocarbon feed mixture boiling over a relatively wide range within the gasoline boiling range and comprising straight chain and non-straight chain hydrocarbons, which process comprises: (1) contacting said mixture with a lean solid granular adsorbent essentially comprising a partially dehydrated zeolitic metallo alumino silicate having substantially uniform pores of about 5 A. in diameter and having adsorbed thereon a displacement exchange fluid of relatively narrow boiling range consisting substantially only of straight chain hydrocarbon components of said feed mixture, whereby there is obtained a raffinate product comprising non-adsorbed non-straight chain hydrocarbon components of the feed mixture in admixture with desorbed displacement exchange fluid, and a rich adsorbent comprising said granular silicate having adsorbed thereon straight chain components of the feed mixture; (2) separating said raffinate product from said rich adsorbent; (3) contacting said rich adsorbent with said displacement exchange fluid whereby the adsorbent is returned to its lean state and there is obtained an extract product comprising desorbed straight chain hydrocarbon components of the feed mixture in admixture with said displacement exchange fluid; (4) separating said extract product from the lean adsorbent; (5) returning the said lean adsorbent obtained in step (4) to step (1); (6) treating the raffinate product obtained in step (2) to separate said non-adsorbed non-straight chain hydrocarbon components of the feed mixture from said displacement exchange fluid; (7) treating the extract product obtained in step (4) to separate therefrom a fraction of relatively narrow boiling range; and (8) returning at least a part of said fraction of relatively narrow boiling range to step (3) as said displacement exchange fluid.

2. A process as defined by claim 1 wherein, in step (1), said feed mixture is maintained in the vapor state and, in step (3), said displacement exchange fluid is maintained in the vapor state.

3. A process as defined by claim 1 wherein at least part of the displacement exchange fluid which separated from the raffinate product in step (6) is returned to step (3).

4. A process as defined by claim 1 wherein the said displacement exchange fluid is a relatively narrow boiling range heart-cut of the said extract product.

5. The process for treating a petroleum hydrocarbon feed mixture comprising straight chain and non-straight chain hydrocarbons containing from 6 to about 9 carbon atoms, including isohexane and n-hexane, which process comprises (1) contacting said mixture with a lean solid granular adsorbent comprising a partially dehydrated zeolitic metallo alumino silicate having substantially uniform pores of about 5 A. in diameter having n-hexane adsorbed thereon, whereby there is obtained a raffinate product comprising non-adsorbed non-straight chain hydrocarbon components of the feed mixture, including isohexane, in admixture with desorbed n-hexane, and a rich adsorbent comprising said granular silicate having adsorbed thereon straight chain components of the feed mixture; (2) separating said raffinate product from said rich adsorbent; (3) contacting said rich adsorbent with n-hexane, whereby the adsorbent is returned to its lean state and there is obtained an extract product comprising desorbed straight chain hydrocarbon components of the feed mixture, including n-hexane; (4) separating said extract product from the adsorbent; (5) returning the said lean adsorbent obtained in step (4) to step (1); (6) distilling the raffinate product obtained in step (2) to obtain a raffinate overhead fraction consisting essentially of isohexane and a raffinate bottom product comprising n-hexane and non-straight chain hydrocarbon components of the feed; (7) distilling said raffinate bottoms product to separate n-hexane therefrom; (8) distilling the extract product obtained in step (4) to separate n-hexane therefrom; and (9) returning separated n-hexane to step (3).

6. The process of treating a petroleum hydrocarbon feed mixture comprising straight chain and non-straight chain hydrocarbons containing from 6 to about 9 carbon atoms, including n-octane, which process comprises (1) contacting said mixture with a lean granular adsorbent comprising a partially dehydrated zeolitic metallo alumino silicate having substantially uniform pores of about 5 A. in diameter having n-octane adsorbed thereon, whereby there is obtained a raffinate product comprising non-adsorbed non-straight chain hydrocarbon components of the feed mixture in admixture with desorbed n-octane, and a rich adsorbent comprising said granular silicate having adsorbed thereon straight-chain hydrocarbon components of the feed mixture; (2) separating said raffinate product from said rich adsorbent; (3) contacting the said rich adsorbent with n-octane, whereby the adsorbent is returned to its lean state and there is obtained an extract product comprising desorbed straight-chain hydrocarbon components of the feed mixture, including n-octane; (4) separating said extract product from the lean adsorbent; (5) returning the said lean

adsorbent to step (1); (6) distilling the raffinate product obtained in step (2) to separate n-octane therefrom; (7) distilling the extract product obtained in step (4) to separate n-octane therefrom; and (8) returning separated n-octane to step (3).

7. A process for treating a petroleum hydrocarbon feed mixture boiling over a relatively wide range within the gasoline boiling range and comprising straight and non-straight chain paraffins and olefines, which process comprises: (1) contacting said feed mixture with a lean first solid granular adsorbent comprising a partially dehydrated zeolitic metallo alumino silicate having substantially uniform pores of about 5 A. in diameter and having adsorbed thereon a first displacement exchange fluid consisting essentially of straight-chain paraffin hydrocarbon components of said feed mixture boiling between relatively narrow limits at the upper end of the boiling range thereof, whereby there is obtained a first raffinate product comprising non-adsorbed non-straight chain hydrocarbon camponents of the feed mixture and non-adsorbed straight chain hydrocarbon components of the feed mixture in admixture with said first displacement exchange fluid, and a rich first adsorbent comprising said granular silicate having adsorbed thereon normal olefine hydrocarbon components of the feed mixture; (2) separating said first raffinate product from said rich adsorbent; (3) contacting said rich first adsorbent with said first displacemnet exchange fluid, whereby there is obtained said lean first adsorbent and a first extract product comprising desorbed normal olefines in admixture with said first displacement exchange fluid; (4) separating said first extract product from said lean first adsorbent; (5) treating the separated first extract product to separate said first displacement exchange fluid therefrom; (6) contacting the separated first raffinate product with a lean second adsorbent comprising a solid granular partially dehydrated zeolitic metallo alumino silicate having substantially uniform pores of about 5 A. in diameter and having adsorbed thereon a second displacement exchange fluid consisting essentially of normal olefine hydrocarbon components of the feed mixture boiling between relatively narrow limits at the lower end of the boiling range thereof, whereby there is obtained a second raffinate product comprising non-absorbed non-straight chain hydrocarbon components of the feed mixture in admixture with said second displacement exchange fluid, and a second rich adsorbent comprising said granular silicate having adsorbed thereon straight chain paraffin hydrocarbon components of the feed mixture; (7) separating said second raffinate product from said second rich adsorbent; (8) contacting said second rich adsorbent with said second displacement exchange fluid, whereby there is obtained said second lean adsorbent and a second extract product comprising desorbed straight chain paraffin hydrocarbon components of the feed mixture in admixture with said second displacement exchange fluid; (9) separating said second extract product from said second lean adsorbent; (10) treating the separated second extract product to separate therefrom as separate entities said second displacement exchange fluid and a fraction consisting essentially of straight-chain paraffin hydrocarbon components of the feed mixture boiling over relatively narrow limits at the upper end of the boiling range thereof; and (11) treating the separated second raffinate product to separate said second displacement exchange fluid therefrom.

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