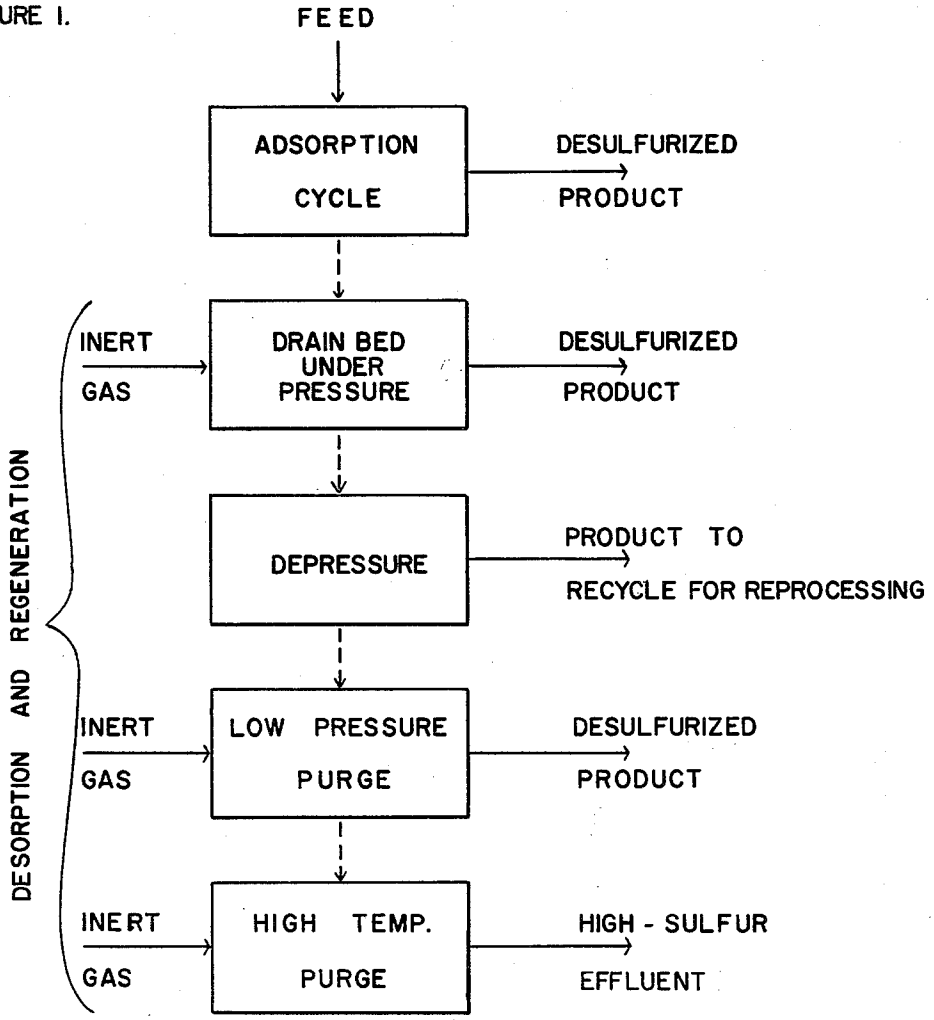
June 8, 1965 K. H. BACON ETAL 3,188,293

PROCESS FOR REGENERATING MOLECULAR SIEVES

Filed March 21, 1962 2 Sheets-Sheet 1

FIGURE I.



INVENTORS
Kenneth H. Bacon
Norman L. Carr
Alfred M. Henke
Harry C. Stauffer

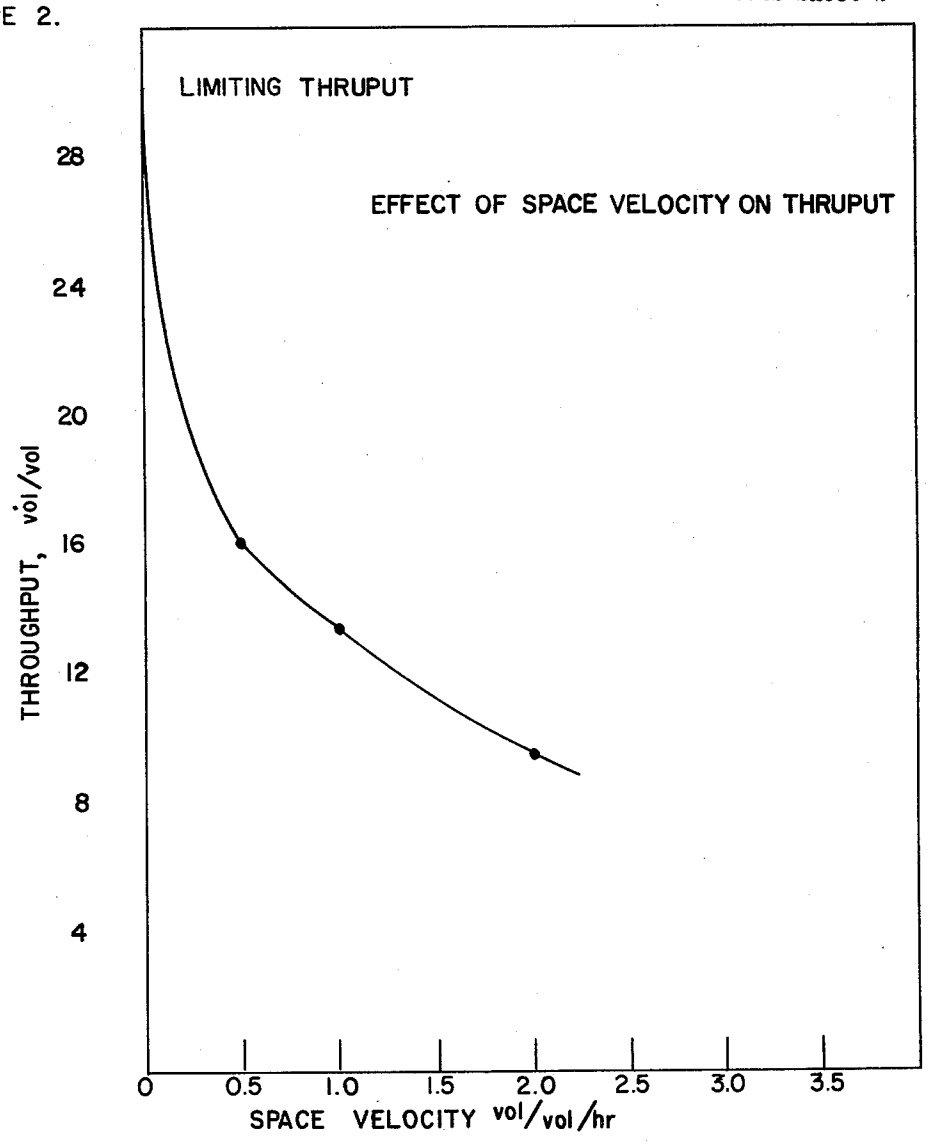
BY

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FIGURE 2.



INVENTORS
Kenneth H. Bacon
Norman L. Carr
Alfred M. Henke
Harry C. Stauffer

BY

United States Patent Office 3,188,293 Patented June 8, 1965

3,188,293
PROCESS FOR REGENERATING MOLECULAR SIEVES

Kenneth H. Bacon, Tulsa, Okla., and Norman L. Carr, Allison Park, Alfred M. Henke, Springdale, and Harry C. Stauffer, Chesnick, Pa., assignors to Gulf Research & Development Company, Pittsburgh, Pa., a corporation of Delaware

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2 Claims. (Cl. 252—411)

This application is a continuation-in-part of our prior co-pending application Serial No. 77,909, filed December 23, 1960, now abandoned and assigned to the same assignee as the present application.

This invention relates to the treatment of hydrocarbon fractions and is more particularly concerned with the treatment of light hydrocarbon fractions, such as gasoline fractions, to remove objectionable sulfur therefrom.

As is known, sulfur is found in varying amounts in petroleum crude oils or fractions thereof. The sulfur may be present in various forms such as free or elemental sulfur or in combined form such as hydrogen sulfide, mercaptan sulfur, thiophenes, or other sulfur compounds of similar cyclic structure. In order that gasoline range boiling petroleum fractions be commercially acceptable, the sulfur content must be relatively low. It is generally accepted that the sulfur content of gasoline be low in order to reduce what is called the octane requirement increase of an engine. It appears necessary to maintain the sulfur content of the gasoline at a low value in order to prevent a marked increase of the octane requirement of an engine after extended use of the engine.

Moreover, various light hydrocarbon fractions such as butane, isopentane, and hexane are widely used in petrochemical applications or as charge stocks in hydrocarbon conversion processes. For such applications it is necessary that the hydrocarbons be essentially sulfur free.

It is a primary object, therefore, of this invention to provide an improved process for treating hydrocarbon fractions to remove sulfur therefrom without regard to the form in which the sulfur is present. The present invention provides an improved process for accomplishing substantially complete desulfurization of light hydrocarbon fractions without regard to the form in which the sulfur is present in the fraction. That is, although it has been suggested (U.S. Patent 2,882,244) that organic sulfur compounds can be selectively adsorbed from mixtures of hydrocarbons of approximately the same composition and degree of unsaturation, it has now been found that sulfur can be removed from hydrocarbon fractions in accordance with this invention without regard to the form in which the sulfur is present in the hydrocarbon fraction.

In accordance with the invention, sulfur is removed from hydrocarbon fractions without regard to the form in which the sulfur is present by a process which comprises contacting said petroleum fractions with a solid alumino-silicate zeolitic adsorbent having a channel diameter of at least 8 Angstroms.

The charge stocks for treatment by the process of this invention may be any sulfur-containing materials, for example light hydrocarbons, petroleum fractions and materials derived from the destructive hydrogenation of coal. It is preferred that the charge stock be a sulfur-containing petroleum fraction. By a sulfur-containing petroleum fraction is meant a whole crude or any fraction thereof which contains sulfur compounds. It is more preferred that the charge stock be a light petroleum fraction boiling between about —65° to 400° F. and includes full range gasolines, natural gasolines and relatively light hydrocarbon fractions, such as butane, isopentane and the like. The process of this invention is particularly advantageous in treating light gasolines boiling in the range from about —44° to 180° F. which materials comprise predominantly hydrocarbon compounds of from about three to six carbon atoms with only minor amounts of lighter and heavier hydrocarbons. Furthermore, it has been found that certain types of compounds found in petroleum fractions tend to be more strongly adsorbed on the adsorbent than the sulfur compounds and, therefore, such charge stocks require much higher adsorbent to charge stock ratios to effect a separation of sulfur compounds. It is, therefore, preferred that the concentration of compounds, which are more strongly adsorbed than sulfur compounds, be kept to a minimum. Unsaturated compounds represent an example of the type of compounds which interfere with the adsorption of sulfur compounds. By an unsaturated compound is meant any hydrocarbon containing a triple or a double bond. Examples of such compounds include acetylenes, aromatics and olefins. By an olefin-type compound is meant a mono olefin, diolefin or cyclic olefin. Specific examples of undesirable unsaturated compounds include 2-butyne; benzene; butylbenzene; naphthalene; cyclohexene; hexene-1; pentene-2; and styrene. It is preferred, therefore, that the charge stock contain less than about 12% total unsaturates with the more preferred charge stock containing less than 6% total unsaturates and with the still more preferred charge stock containing less than 1% total unsaturates.

The solid alumino silicate adsorbents which are employed in the practice of the invention are those crystalline dehydrated zeolites, natural or synthetic, having a well-defined physical structure which are known as "molecular sieves."

Chemically these molecular sieve zeolites are hydrous alumino-silicates generally containing one or more sodium, potassium, strontium, calcium, or barium cations, although zeolites containing hydrogen, ammonium, or other metal cations are also known. These zeolites have a characteristic three-dimensional, alumino-silicate anionic network, the cations neutralizing the anionic charge. Upon dehydration, the three-dimensional lattice network of the crystal is maintained, leaving intercommunicating channels, pores, or interstices of molecular dimensions within the crystal lattice. The cross-sectional diameter of such channels can vary, dehydrated three-dimensional zeolites having channels with various cross-sectional diameters being known. However, for each zeolite of this type, the narrowest cross-sectional diameter of the channels is a characteristic and is substantially uniform and fixed throughout the crystal. Thus, materials are available having channel diameters of substantially all 4 Angstrom units, all 5 Angstrom units, etc., as the case may be. It is, therefore, conventional in the art to characterize the crystalline, dehydrated, three-dimensional zeolites as molecular sieves of a definite channel diameter, for example, molecular sieves having a channel diameter of 5 Angstrom units, or even more simply, 5 Angstrom molecular sieves. Such molecular sieve adsorbents are presently available items of commerce marketed by Linde Air Products Company, 30 East 42nd Street, New York, New York. For the purposes of the present invention the zeolitic adsorbents employed must exhibit a high and selective adsorptive capacity for sulfur or sulfur compounds and must have a channel diameter of sufficient size to permit entry of these materials. Thus, for the purposes of the invention the molecular sieve adsorbents employed should have a substantially uniform channel diameter of at least 8 Angstrom units and preferably greater. The preferred zeolite of this invention is a

"13X" molecular sieve marketed by Linde. U.S. Patent 2,983,670 to Seubold, Jr. indicates the "X" type zeolite has a relatively uniform pore diameter within the range of about 11 to 14° Angstrom. For the manner of preparation of the "X" zeolites, reference is made to U.S. Patent 2,882,244 to Robert M. Milton which describes the preparation of several different types, any of which may be used herein provided the average pore diameter of the zeolite is at least 8° Angstrom.

Referring now to FIGURE 1 of the drawings, which sets forth in a block diagram various embodiments of the practice of the invention, a sulfur-containing hydrocarbon fraction such as a natural gasoline is contacted with a molecular sieve adsorbent having a channel diameter of sufficient size to permit pore adsorption of the sulfur compounds contained in the feed. The contact of the petroleum feed with the selected solid adsorbent can be effected by various means. For example, liquid fresh feed is contacted with the solid particle selective adsorbent preferably in the form of a fixed bed, a moving bed, a slurry bed or a fluidized bed, and the hydrocarbon charge material may pass in direct, concurrent or counter-current contact with the molecular sieve adsorbent. The molecular sieve adsorbent is preferably maintained in a finely pelletized or extruded form such as 1/16 or 1/4 inch average maximum diameter.

Any adsorption temperature may be employed. The lower adsorption temperature is limited only by the freezing point of the charge stock. The upper temperature is limited by the decomposition of the materials being adsorbed or the decomposition of the adsorbent itself. Lower temperatures of adsorption are preferred since higher throughputs are achieved before regeneration of the adsorbent is required. Temperatures within the range of about −20° to 350° F. may, therefore, be employed. It is preferred, however, that temperatures from about 0° to 180° F. be employed, while it is still more preferred to employ temperatures from about 30° to 100° F. While the adsorption of sulfur compounds may take place with the charge stock either in the vapor or the liquid state, it is preferred to maintain the charge stock in the liquid phase during the adsorption operation. Therefore, the pressure during the adsorption operation is maintained sufficiently high so as to exceed the vapor pressure of the charge stock at the operating temperature.

In simple fixed bed operation the sulfur undergoing adsorption is removed continually from the gasoline feed stock and accumulates within the pores and on the surface of the adsorbent. In a typical adsorption operation the effluent is free of sulfur at the start of the cycle. At some point in the cycle depending upon operating conditions such as temperature, flow rate, and adsorption column design, sulfur compounds begin to appear in the effluent. After this the concentration of sulfur in the effluent from the adsorption treatment gradually increases. Continued operation results in an increasing amount of sulfur in the effluent until the adsorption column effluent reaches the feed concentration. The point in the effluent concentration history at which the sulfur reaches some predetermined desired level is termed the breakthrough time or volume. The breakthrough volume can be predetermined so that sulfur is removed to a desired extent and the effluent hydrocarbon stream meets a predetermined specification.

The volume of charge stock which can be treated per volume of adsorbent before the breakthrough volume is reached is termed the throughput. Throughput will also, of course, depend to a large extent on the nature of the charge stock and the extent of removal of sulfur compounds which is desired. It is desirable, of course, to obtain as high a throughput as possible before it becomes necessary to regenerate the adsorbent. It has been found that increased throughputs may be achieved by operating at lower adsorption temperatures with the feed in the liquid phase and also by operating at the proper space velocity. In general, the liquid hourly space velocity, that is, the liquid volume of charge stock per volume of adsorbent per hour which may be employed may vary over a wide range, for example, from 0.1 to 20 or more with preferred liquid hourly space velocities depending to a large extent on the nature of the charge stock. For example, it has been found that when light hydrocarbons (such as propane) containing small amounts of sulfur compounds are treated, preferred space velocities are between 1 and 15; whereas, when certain natural gasolines containing about 580 p.p.m. of mercaptan sulfur are treated, the preferred space velocities are between about 0.1 and 3 with still more preferred space velocities between 0.3 and 1. Thus, the curve in FIGURE 2 illustrates the effect of space velocity on throughput for a natural gasoline containing about 580 p.p.m. of mercaptan sulfur. It should be understood that the curve in FIGURE 2 is typical of the effect of space velocity on throughput, but the absolute numbers for space velocity and throughput are valid only for the particular charge stock for which the curve was obtained. The curve in FIGURE 2 was obtained by treating at a temperature of 80° F. and a pressure of one atmosphere a gasoline petroleum fraction containing about 580 p.p.m. of mercaptan sulfur to produce an effluent gasoline containing not more than 6 p.p.m. of mercaptan sulfur. As is seen from the typical curve, as the space velocity increases the throughput of the process rapidly decreases.

After the desired breakthrough point is attained, that is, when the concentration of sulfur in the effluent from the adsorption operation increases to a value approaching the maximum permissible limit to meet required specifications, introduction of the feed to the adsorption zone is discontinued and the molecular sieve adsorbent is desorbed and regenerated for reuse. Desorption and regeneration of the adsorbent can be accomplished by several conventional procedures known to the art, for example, purge gas stripping, displacement, and thermal-pressure swing techniques. A particularly preferred and unique procedure for desorption and regeneration of the molecular sieve adsorbent is described in detail below as a preferred embodiment of the invention. This preferred procedure provides important advantages with respect to maintenance of long adsorbent life and low feed stock loss, which features are of great importance from a commerical viewpoint. The preferred desorption and regeneration procedure in accordance with the invention involves the following sequence of operations: (1) a high pressure gas displacement of occluded liquid in the adsorbent bed; (2) depressurization of the adsorbent bed; (3) low pressure gas purge of the adsorbent bed; and (4) high temperature gas purge of the adsorbent bed.

In the first step of the desorption procedure, an inert gas is introduced into the adsorbent bed to remove liquid which is occluded within the void spaces of the sorbent mass. An inert gas such as nitrogen, helium, carbon dioxide, natural gas, and the like is suitable for this purpose. This operation is conducted at a temperature in the range of from about 0° to 100° F. and at a relatively high pressure in the range of about 50 to 500 p.s.i.g. The liquid removed from the bed during this operation has a relatively low sulfur content and may be admixed with the treated gasoline product originally recovered from the adsorption operation to increase the yield of low sulfur content gasoline. After the adsorbent bed has been substantially completely drained of occluded liquid the bed is depressured to a pressure generally not exceeding about 1 atmosphere, while the temperature is maintained in the range of about 0° to 100° F. The liquid effluent obtained upon depressurization of the adsorbent bed contains some sulfur and generally exceeds specifications so that it is recycled for admixture with additional fresh feed stock which is to be treated according to the invention. Following depressurization of the bed the molecular sieve adsorbent is subjected to a low pressure purge with an inert gas. The same inert gases as previously mentioned are

suitable. This low pressure purging operation is conducted at a temperature in the range of 0° to 100° F. and a pressure not exceeding about 50 p.s.i.g. The liquid effluent or desorbate obtained by this operation contains surprisingly little or no sulfur and can therefore be admixed with the treated product originally recovered to increase the yield of low-sulfur content gasoline. The final step in the desorption-regeneration procedure involves purging the adsorbent with the inert gas at a relatively high temperature to remove from the pores of the adsorbent the sulfur contained therein. This purging operation is carried out with an inert gas, such as those previously described, at a pressure of about one atmosphere and a temperature of from about 400° to 850° F. As a result of this treatment substantially all of the sulfur which has been adsorbed within the pores of the molecular sieve adsorbent is removed therefrom and the adsorbent is ready for use in treating additional fresh feed. The sulfur obtained from desorbing the adsorbent can of course be sent to storage or subjected to further processing as desired.

The following examples further illustrate the process of the invention and its advantages.

EXAMPLE 1

A de-ethanized natural gasoline having an approximate composition:

Table I

Component:	Percent by weight
Ethane	2.0
Propane	19.3
Isobutane	11.3
n-Butane	27.4
Isopentane	11.8
n-Pentane	10.0
Hexanes	9.6
Heptanes	4.6
Octanes	3.8
Nonanes	0.2

and a sulfur content of 850 p.p.m. of mercaptan sulfur was treated in accordance with the invention. The raw gasoline was fed into an adsorption column 2.07 inches I.D. and 24 inches in length containing a "13X" molecular sieve adsorbent. The molecular sieve adsorbent employed is marketed by Linde Air Products Company, East 42nd Street, New York, New York under the name "13X Molecular Sieve." As noted earlier, the "13X" molecular sieve has a relatively uniform pore diameter within the range of 11 to 14° Angstrom. The molecular sieve is employed in a fixed bed in pellets of approximately ⅛ inch diameter. The temperature of the adsorption column was maintained at 100° F. and the total pressure at 350 p.s.i.g. The raw gasoline was introduced into the top of the adsorption column at a rate to provide a space velocity of 2.9 volumes liquid gasoline per hour per volume of adsorbent in the column. The gasoline flowed downwardly through the molecular sieve adsorbent and the effluent was continuously removed from the bottom of the adsorption column and analyzed for sulfur content. After approximately 4.4 hours of continuous operation the concentration of mercaptan sulfur in the effluent gradually began to approach a value of 10 p.p.m. At this point, the breakthrough point, introduction of the feed gasoline was discontinued.

EXAMPLE 2

The procedure described in Example 1 was repeated employing similar operating conditions, that is, a pressure of 350 p.s.i.g., a space velocity of 2.8 volumes of gasoline per hour per volume of adsorbent, but the temperature was increased to 180° F. In this case the throughput expressed as volumes of gasoline per volume of adsorbent was reduced to 7.3 as compared to a throughput of 11.3 as obtained in Example 1.

In other runs employing approximately the same pressure and space velocity but an operating temperature in the adsorption zone of about 375° F., the throughput was reduced to 3.2 volumes of feed per volume of adsorbent.

EXAMPLE 3

A kerosene petroleum fraction of 45.8° A.P.I. and boiling in the range of 380° to 5.36° F. was passed upflow at atmospheric pressure, a 1.0 liquid weight hourly space velocity and a temperature of 75° to 80° F. through a one inch I.D. and 48 inch long column of 1/16 inch Linde "13X" molecular sieves which had been preactivated by heating at 650° F. for four hours. Charge and product inspections are given on Table II below.

Table II

Inspections	Kerosene Charge	Product
Sulfur: p.p.m.:		
Total	700	230
Mercaptans	333	93
Fluorescent Indicator Analysis:		
Olefins	1.2	1.0
Aromatics	9.9	3.9
Saturates	88.9	95.1

This example shows that a higher boiling, high unsaturate content charge can be treated to lower the sulfur content thereof.

EXAMPLE 4

A gasoline similar in composition to that of Example 1 was treated in an adsorption zone containing Linde "13X" molecular sieves. This raw gasoline contained 2260 p.p.m. of both mercaptan and sulfide sulfur. The adsorption zone was maintained at a temperature of 100° F. and a total pressure of 350 p.s.i.g., and the raw gasoline was introduced at a space velocity of 1.7 volumes of gasoline per hour per volume of adsorbent. After approximately 13 hours of operation, analysis of the effluent from the adsorption column showed the sulfur content to be less than 25 p.p.m. sulfur which is considered the desired sulfur breakthrough point. Introduction of the gasoline feed was then discontinued and desorption and regeneration of the adsorbent was initiated. Nitrogen at 350 p.s.i.g. was introduced into the feed inlet at the top of the adsorption column to remove occluded liquid from the adsorbent while the bed was maintained at a temperature of 100° F. The rate of liquid withdrawal approximated the liquid charge rate during the adsorption cycle. The liquid obtained from this operation was admixed with the treated gasoline originally recovered from the primary adsorption step. Nitrogen flow was then discontinued and the column was depressurized from the bottom to one atmosphere. The condensed liquid was collected and recycled for admixture with fresh feed. Nitrogen was again introduced into the top of the column at a rate to provide a spaced velocity (S.T.P.) of 63 volumes of nitrogen per hour per volume of adsorbent. The adsorption column was maintained at atmospheric pressure and a temperature of 100° F. during this operation which continued for approximately 35 minutes. The desorbate obtained had a sulfur content appreciably lower than that required by specifications and was admixed with the principal treated gasoline product. The adsorbent bed was then gradually heated to a maximum temperature of about 690° F. while passing nitrogen upwardly through the bed at a space velocity of 63 (S.T.P.) to desorb the more strongly held constituents from the molecular sieves. This high temperature gas purge operation took approximately five hours at which time the molecular sieve adsorbent was substantially completely desorbed and ready for use in treating additional fresh feed. The sulfur obtained from this high temperature purge was sent to storage for further processing.

Analysis of the total recovered gasoline fraction showed

the total sulfur content to be less than 25 p.p.m. total sulfur which represents a sulfur removal of 97 percent. The yield of gasoline was 99.7 percent by volume of charge.

The process of the invention may be carried out in a continuous manner by employing a plurality of sulfur adsorption units, one or more adsorbers onstream and one or more adsorbers undergoing desorption and regeneration at the same time. In the light of the foregoing clear disclosure, the manner of employing one or more sulfur adsorption units in the practice of the invention is deemed to be obvious to those skilled in the art.

From the foregoing description it is apparent that the invention is directed to an improved and highly advantageous method of removing undesirable sulfur from petroleum fractions. In treating petroleum fractions in accordance with the invention sulfur is effectively removed therefrom without the employment of extreme operating conditions which would deleteriously affect the composition or properties of the hydrocarbon charge material. The process of the invention is characterized also in the low liquid losses experienced and high yields of low-sulfur content product which is achieved.

It is believed apparent to one desiring to practice the invention that a particular hydrocarbon mixture, if desired, can be fractionated into specific fractions prior to desulfurization. For example, a natural gasoline could be distilled to obtain such fractions as propane, butane, isopentane, and so forth, which fractions could then be treated individually by the process of the invention.

Those modifications and equivalents which fall within the spirit of the invention and the scope of the appended claims are to be considered part of the invention.

We claim:

1. A process for regenerating molecular sieves used in an adsorption zone for the removal of sulfur which comprises:

(1) passing an inert gas through the adsorption zone at a temperature from about 0° to 100° F. and a pressure of 50 to 500 p.s.i.g., and recovering an effluent of low sulfur content;

(2) reducing the pressure in the adsorption zone to about one atmosphere while maintaining the temperature therein at from 0° to 100° F. to recover a high sulfur content effluent;

(3) passing an inert gas through the adsorption zone at a temperature of 0° to 100° F. and a pressure not above about 50 p.s.i.g. to recover a low sulfur content effluent; and then

(4) passing an inert gas through said adsorption zone at a temperature of from about 400° to 850° F. and a pressure of about one atmosphere to recover a sulfur-rich effluent.

2. A process according to claim 1 wherein the molecular sieves have a channel diameter of at least 8 Angstroms.

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ALPHONSO D. SULLIVAN, *Primary Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,188,293 June 8, 196

Kenneth H. Bacon et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 8, for "5.36° F." read -- 536° F. --; sam column 6, line 57, for "spaced" read -- space --.

Signed and sealed this 18th day of January 1966.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents