June 6, 1961 F. T. EGGERTSEN 2,987,471

SEPARATION OF HYDROCARBONS

Filed Nov. 19, 1956 2 Sheets-Sheet 1

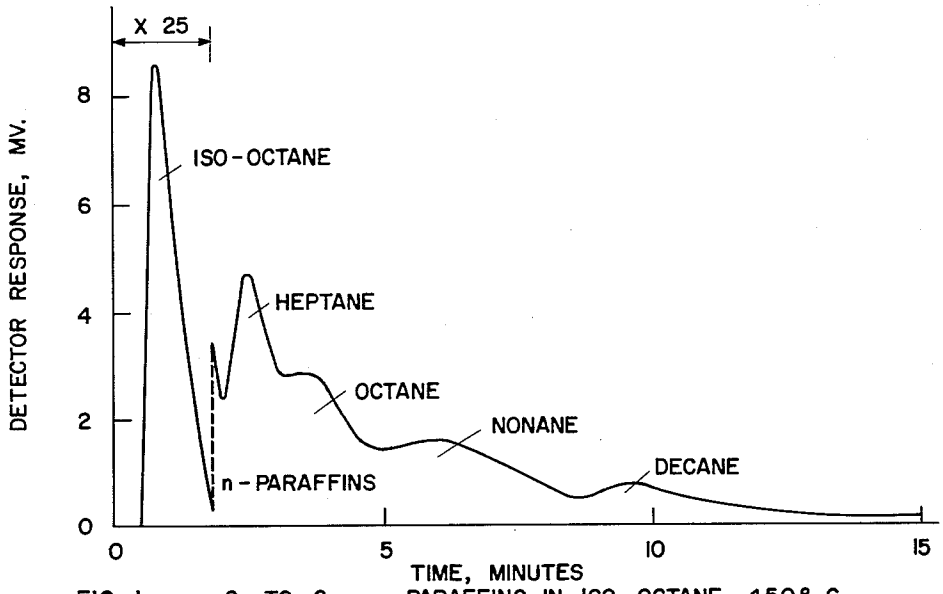


FIG. 1 C_7 TO C_{10} n-PARAFFINS IN ISO-OCTANE, 450° C

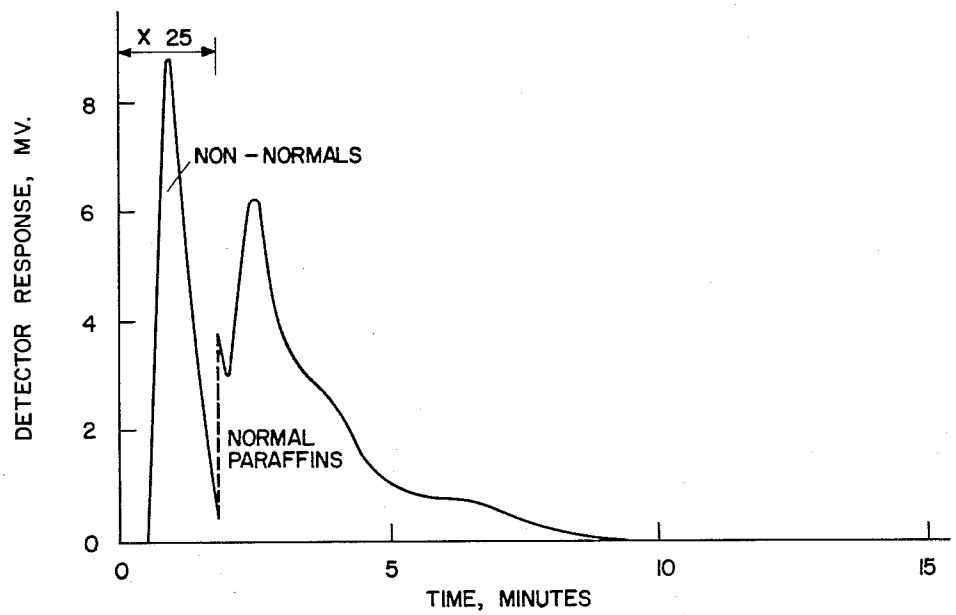


FIG. 3 COMMERCIAL REFORMATE, 450° C

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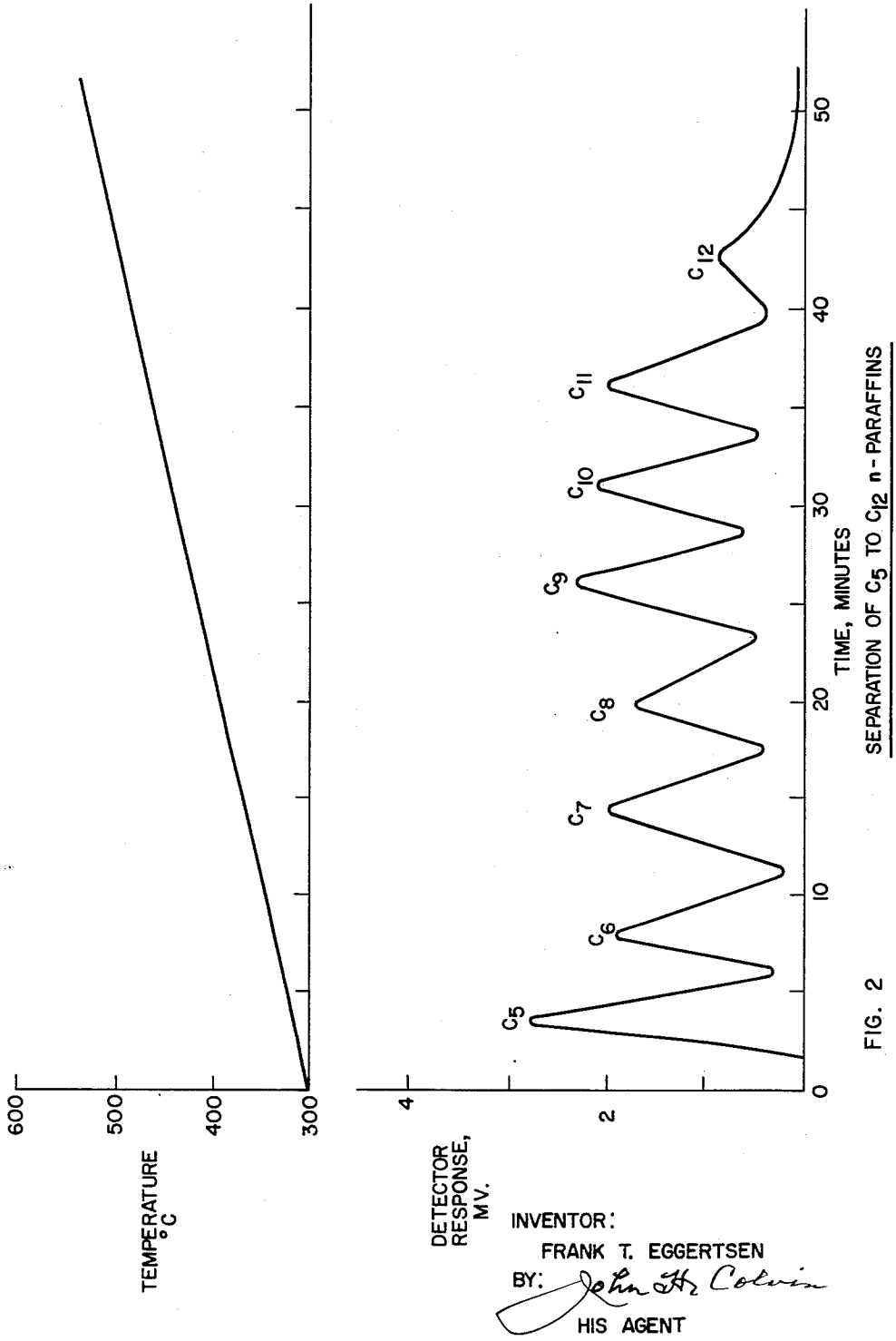


FIG. 2

SEPARATION OF C_5 TO C_{12} n-PARAFFINS

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United States Patent Office 2,987,471
Patented June 6, 1961

2,987,471

SEPARATION OF HYDROCARBONS

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Filed Nov. 19, 1956, Ser. No. 622,893
1 Claim. (Cl. 208—310)

This invention relates to a process for the separation of normal hydrocarbons from non-straight-chain hydrocarbons. It relates more particularly to the separation of vapor mixtures of normally liquid hydrocarbons which are substantially thermally stable at a temperature of at least about 380° C.

Various methods have been proposed heretofore to separate aromatic hydrocarbons from non-aromatic hydrocarbons, such as liquid-liquid solvent extraction, extractive distillation, azeotropic distillation and selective adsorption. These methods have been developed to commercial scale operations. However, except in special cases, equally satisfactory processes for the separation of straight-chain hydrocarbons from non-straight-chain hydrocarbons have not been made available.

Normal paraffins are frequently undesired components in hydrocarbon fuels and lubricants: they depress the octane number of gasoline, raise the pour point of lubricating oil and raise the freezing point of diesel and jet fuels.

It has been proposed to utilize certain natural and synthetic zeolites having rigid three-dimensional anionic networks and having interstitial channels sufficiently large to accommodate straight-chain hydrocarbons but sufficiently small to exclude the branched-chain and/or cyclic hydrocarbons, to separate the straight-chain hydrocarbons from other hydrocarbons (Barrer, U.S. 2,306,610). Although the normal hydrocarbons are selectively sorbed by such solid substances, no commercially feasible process has been developed to utilize this separation effect.

A principal object of the present invention is to provide an improved process for the separation of normal hydrocarbons, saturated or unsaturated, and particularly normal paraffins, from branched-chain and/or cyclic hydrocarbons. A more specific object is to provide a process for the separation of straight-chain hydrocarbons containing from four to about twenty carbon atoms per molecule from non-straight-chain hydrocarbons. Still more specifically, it is an object of the invention to provide an improved process for the separation of normally liquid normal hydrocarbons from similarly boiling non-straight-chain hydrocarbons. It is a further specific object to provide a process in which normal paraffin fractions of different carbon numbers are separately recovered from admixtures with other hydrocarbons. These objects will be better understood and others will appear to those skilled in this art from the more detailed description of the invention, which will be made with reference in part to the accompanying drawing, wherein:

FIG. 1 is a graph showing the separation at 450° C. of C_7 to C_{10} normal paraffins from 2,2,4-trimethylpentane, the so-called isooctane of commerce.

FIG. 2 is a graph showing the separation of a mixture of normal paraffins.

FIG. 3 shows the separation at 450° C. of normal paraffins from other components in a commercial naphtha reformate.

Zeolites having rigid three-dimensional anionic networks and having intracrystalline interstitial channels whose narrowest cross-section has essentially a uniform diameter, e.g., about 4 or about 5 Angstrom units, are well known to the art. They are commonly designated "molecular sieves." The intracrystalline channels are generally designated "pores." Such zeolites are described,

for example, in a paper entitled "Zeolites as Absorbents and Molecular Sieves," by R. M. Barrer, in "Annual Reports on the Progress of Chemistry for 1944," vol. 61, pp. 31–46, London (1945). More recently certain synthetic molecular sieves have become commercially available from Linde Air Products Company. One such molecular sieve is designated MS–4A. It is a zeolite of average composition $0.96\pm0.04\ Na_2O.1.00\ Al_2O_3.1.92\pm0.09\ SiO_2$ plus an amount of water depending on the degree of dehydration; the crystals are cubic, with unit cells measuring, on an edge, approximately 12.26 Angstrom units, and are characterized by an essentially uniform pore diameter of about 4 Angstrom units. Another available sieve is designated MS–5A. This is made from MS–4A by replacement of approximately 75% of the sodium ions with calcium ions by ion exchange. These are also cubic crystals, having the same unit cell dimensions as MS–4A, and are characterized by an essentially uniform pore diameter of about 5 Angstrom units.

Zeolites become active for selective sorption by a treatment designed to drive off the water originally present in the interstitial spaces. The spaces vacated remain and become available for the sorption of compounds of appropriate maximum critical molecular cross-section. The zeolites may be subjected to temperatures of 600° C. and, in some cases up to 800° C. or more without destruction of their crystalline structure. In some cases, repeated contact with steam can be tolerated without substantially affecting their structure.

Activated zeolites are generally soft, friable materials. Although they may be used as sorbents in pure form, if carefully handled, they can be made up in the form of particles held in shape by the addition of ten to twenty percent of an inert binder material such as clay. They may also be used admixed with other solids which are stable at the conditions to be used in the process and which are, preferably, non-adsorbents or relatively non-selective adsorbents so as not to interfere in the desired separations.

The basis for the separation of the normal hydrocarbons from hydrocarbon mixtures containing them and non-straight-chain hydrocarbons which is effected by these natural or synthetic zeolites appears to be that the normal hydrocarbons are capable of passing into and through the interstitial openings (pores) of the sorbent, whereas the non-straight-chain hydrocarbons have too large a maximum cross-sectional diameter to do so. This is supported by the results and the following approximate largest cross-sectional dimensions perpendicular to the longitudinal axes, sometimes designated "critical cross-sections," as determined by the use of Fischer-Hirschfelder scale models, reputed to give fair estimates of molecular size, of some representative hydrocarbons: n-paraffins, 4.9 Angstroms; monomethylparaffins, 6.3 Angstroms; gem-dimethylparaffins, 6.7 Angstroms; ethylparaffins, 7.2 Angstroms; cyclohexane, 6.6 Angstroms; and benzene, 6.9 Angstroms. These differences in critical cross-section permit the separation of normal hydrocarbons from branched and cyclic hydrocarbons by sorption in molecular sieves whose pore diameters are sufficiently large to admit the normal hydrocarbons but not large enough to admit the other types. Thus, chabazite, gmelinite and a synthetic zeolite of formula $BaAl_2Si_4O_{12},nH_2O$ have been reported to have diameters of the narrowest pore cross-sections between 4.89 and 5.58 Angstrom units. These sieves, as well as Linde MS–5A, occlude normal hydrocarbons and do not occlude non-normals; hence they permit the described separations to be made. Mordenite has been reported to have a corresponding pore diameter between 4.0 and 4.89 Angstrom units. It, as well as Linde MS–4A, does not occlude even normal hydrocarbons

having four or more carbon atoms. It does sorb methane and ethane, with which the present invention is not concerned.

It should be understood that pore diameters herein referred to, which are determined by physical measurements such as X-ray methods or by the sorptive characteristics of the zeolites, may not be precisely accurate numbers. Also, it has been found that normal hydrocarbon molecules may enter pores whose maximum diameters are believed to be at least slightly smaller than the apparent maximum critical cross-section diameter of the molecule. For purposes of this invention, reference to zeolites having substantially uniform intracrystalline interstitial channels (or pores) of from about 5 to about 6 Angstrom units diameter includes those above-mentioned zeolites and others which have the characteristic of selectively sorbing normal hydrocarbons of four or more carbon atoms per molecule and not sorbing non-normals, by virtue of their crystal structure. These sorbents may also be referred to herein as zeolitic molecular sieves of from about 5 to about 6 Angstrom unit maximum pore diameter.

The necessity for substantial uniformity of the maximum pore diameters is demonstrated by the fact that when a silica gel having the same average pore diameter as the molecular sieve, but a distribution of sizes including substantial proportions both of smaller and larger pores, is used in the place of the molecular sieve, a suitable separation is not obtained.

While the ability of certain molecular sieves to sorb straight-chain hydrocarbons from mixture with other hydrocarbons, generally in static liquid and vapor systems and at temperatures up to about 350° C., has been known, it has now been found that by operating at a temperature of from about 380° C. to about 600° C., preferably at least 400° C. and still more preferably from about 450° C. to about 500° C., zeolites having rigid three-dimensional anionic networks and having substantially uniform intracrystalline interstitial channels of from about 5 to about 6 Angstrom unit diameter sorb normal hydrocarbons sufficiently rapidly and sufficiently strongly to permit their separation from admixture with other hydrocarbons by passing the hydrocarbon mixture through a mass of the solid material at a relatively high space velocity in vapor phase. Although the normal paraffins are sufficiently sorbed at this high temperature while the other hydrocarbons pass through the solid mass with sufficient ease, the sorbed normal hydrocarbons are merely delayed in their transit and can be quickly and substantially completely separated from the solid shortly thereafter. This makes it possible to repeat the cycle of operations sufficiently often to provide for separations at a rate comparable to that of solvent extraction and the like.

Although it has been shown before that prepared zeolites of substantially uniform 5 Angstroms pore diameter sorb normal paraffins at a temperature as high as 350° C., it is surprising to find that the normal paraffins are still sorbed sufficiently at higher temperatures above about 380° C., and substantially atmospheric pressure, especially as high as from 450° to 500° C., and yet they are displaced so readily at the same temperature and pressure as to make their recovery from the sorbent quick and essentially complete without the necessity to heat the sorbent to a still higher temperature.

This is demonstrated by the results shown in Table I for relative initial and complete emergence times, at one atmosphere pressure, of normal paraffins, a normal olefin and representative cyclic and branched-chain saturated and olefinic hydrocarbons through a thermostated column of Linde MS–5A molecular sieve material. Helium was used throughout the separation as a sweeping gas at a constant rate. Thermal conductivity was employed to detect the hydrocarbons as they emerged from the column. Each hydrocarbon was charged to the column as a pure compound in a separate run. The hydrocarbon was added to the column by diverting the flow of helium through the hydrocarbon container to push the liquid hydrocarbon charge into the column. The hydrocarbon was quickly vaporized. A small amount of air associated with it was pushed through the column ahead of sorbed hydrocarbon. The recording peak resulting from emergence of this air was used as the reference point to measure emergence time. This peak appeared in 0.5 minute from the time of charging. The non-normal hydrocarbons began to emerge from the column with the air peak. Hence, their initial emergence time was zero.

Table I

Sorbent.....900 mg. MS–5A (3" x ¼" column).
Sample.....ca. 5 mg.
Sweeping gas...35 ml./min.

Temperature, °C.	300	400	450	500	300	400	450	500
Substance	Initial Emergence Time, min.				Substantially Complete Emergence Time, min.			
n-pentane	1.5				7			
n-hexane	5	0.3	0.1		15	3	2	
hexene-1			0.3				2	
n-octane	>30	1.5	0.6	0.1		8	4	2
n-decane		15	4	0.4			12	4
n-dodecane			15	2.5				12
2-methylbutene-1 4-methylpentene-2 cyclohexene benzene 2,2,4-trimethylpentane o-xylene	0.0				ca. 1 min.			

Whereas the non-straight-chain hydrocarbons emerged substantially completely within 1 minute even at the lowest temperature, the normal hydrocarbons required a longer time depending on carbon number. The data show that it is feasible to sorb straight-chain hydrocarbons at a temperature in the range of 380° C. to 500° C. By operating at temperatures above about 400° C. the subsequent period required to remove the normal hydrocarbons is materially reduced.

The data in Table I also demonstrate that the initial emergence time for normal hydrocarbons increases rapidly with increase in the length of the chain, i.e., increase in carbon number of the molecule at otherwise equal conditions, although it does not vary for non-straight-chain hydrocarbons. Therefore, practical considerations for large scale application require that the conditions of operation, such as temperature, ratio of solid-to-hydrocarbon, length of column and rate of flow of sweeping gas are correlated to give an initial emergence time for the lightest normal hydrocarbon to be separated sufficiently greater than the essentially complete emergence time of the non-straight-chain hydrocarbons that satisfactory separation between them is obtained and yet the heaviest normal hydrocarbon is sufficiently emerged (eluted) within a reasonably short time thereafter. The time for emergence of the major portion of the heaviest normal hydrocarbon should not be more than about 200 times that of the lightest one to be separated, better still no more than 100 times as much, and preferably no more than about 50 times as much.

The temperature may be raised to reduce the emergence or elution time, but this has the disadvantage of greater danger of thermal degradation of the hydrocarbon. Therefore, it is preferred to minimize this elution time differential by providing mixtures to be separated which have relatively narrow boiling ranges.

The boiling points at atmospheric pressure of normal paraffins, from butane through eicosane, are listed in Table II, as well as the difference in boiling point between each paraffin and the next higher one (Δ° C.). The "carbon number" is the number of carbon atoms per molecule.

Table II

Carbon Number	Paraffin	B.P.,° C.	Δ° C.
4	Butane	0.5	35
5	Pentane	36	33
6	Hexane	69	29
7	Heptane	98	28
8	Octane	126	25
9	Nonane	151	23
10	Decane	174	22
11	Hendecane	196	22
12	Dodecane	216	19
13	Tridecane	235	19
14	Tetradecane	254	17
15	Pentadecane	271	16
16	Hexadecane	287	15
17	Heptadecane	302	14
18	Octadecane	316	14
19	Nonadecane	330	13
20	Eicosane	343	

Boiling ranges of feeds in the process of this invention should be generally no more than 125° C. and preferably less than 100° C. The difference in carbon-atoms-per-molecule—designated "carbon number spread" and symbolized by Δn— between the lowest boiling and highest boiling normal hydrocarbon in the fraction should be no more than 5, and preferably no more than 2, when rapid recovery of normal hydrocarbon is desired. Fractions with larger carbon number spread can be charged when it is desired to recover each of the normal hydrocarbons as a separate cut, using a larger desorption period.

To illustrate, a hydrocarbon mixture containing n-hexane and n-heptane as the only normal paraffins and various other hydrocarbons has a carbon number spread of one ($\Delta n=7-6=1$) and may have any boiling range which encompasses the boiling points of n-hexane (69° C.) and n-heptane (98° C.) but excludes essentially the boiling points of n-pentane (36° C.) and n-octane (126° C.) and preferably differs from these by at least about 5° C. Thus, the boiling range of the mixture may range from an initial boiling point of from about 41° to 68° C. to an end boiling point of from about 99° to about 120° C. The minimum boiling range of this feed, therefore, is about 31° and the maximum range is about 79° C.; to be sure that the desired normal paraffins are included and undesired ones excluded it is preferred to have a minimum boiling range of at least about 35° C. and a maximum range of no more than about 75° C. The temperature at which normal paraffins present in a hydrocarbon mixture boil may be shifted by azeotroping effects due to aromatic or other non-paraffinic hydrocarbons in the mixture. This will result in shifting the boiling points somewhat from those given in Table II, but will not substantially change the range which may be used. In any event, analytical tools available today, e.g. the mass spectrometer, make it readily possible to determine what cut points must be used to produce a feed stock having any desired carbon number spread in the normal hydrocarbon components.

In some cases it will be desired to separate only one or less than all of the higher boiling normal hydrocarbons of a hydrocarbon mixture from the other hydrocarbons. In that case the presence of lower boiling normal hydrocarbons is not objectionable and the initial boiling point of the mixture may be correspondingly lower to include lighter normal hydrocarbons; a substantial portion of the lighter normal hydrocarbons, which have a relatively lower emergence time than the heavier ones, may be eluted into the product stream which is enriched in non-straight-chain hydrocarbons. Thus, the so-called cut point may be delayed until a portion of the lower normal hydrocarbons is removed as effluent with the non-normal hydrocarbons. This may be particularly advantageous in processing gasoline fractions where the higher normal paraffins are advantageously removed but the lower normal paraffins, e.g. C_4 and C_5 may be desired in the product.

The separation of C_7 to C_{10} normal paraffins ($\Delta n=3$)

from isooctane at 450° C., in a mixture containing 2.3% wt. each of the normals, is presented graphically in FIG. 1. Isooctane emerged completely in less than two minutes, as it flashed through the sorbent mass (Linde MS–5A) without any observable retardation while the normal paraffins emerged soon afterwards over a period of about twelve minutes.

FIG. 2 illustrates differences in elution times for individual normal paraffins in a C_5–C_{12} mixture of normal paraffins. An inert gas stream was passed through a heated column of Linde MS–5A; the mixture of paraffins was added to the gas stream ahead of the column of sorbent during a period of a few seconds. The column was gradually heated from 300° to over 500° C., as indicated by the straight line graph.

FIG. 3 shows a typical result obtained at 450° C., for the separation by a 5 Angstrom unit molecular sieve of normal paraffins in a commercial reformate which contained essentially C_7 through C_{10} hydrocarbons.

The amount of sorbent for the above separations was 900 mg. and the flow rate of (helium) stripping gas 30 to 40 ml. per minute. At lower flow rates the sorbent retains normals still longer, making it easier to separate them from non-normals which are flash-distilled from the sorbent column.

At 450° C. and one atmosphere pressure with the above flow rate of stripping gas, 300 parts by weight of the MS–5A sorbent will retard about 7 parts by weight of n-hexane or 15 parts by weight of n-decane so that they emerge after isooctane.

In another series of experiments on a larger scale of operation and at 500° C. and using in some cases nitrogen and in others methane as sweep gas, a dehexanized portion of the same commercial naphtha reformate was separated over Linde MS–5A molecular sieve. The hydrocarbon mixture had a boiling range of from about 75° to about 170° C. It was a mixture of aromatic, naphthenic, isoparaffinic and normal paraffinic hydrocarbons, with the normal paraffins ranging from 7 to 10 carbon atoms per molecule. The approximate composition on a weight basis was: 9% normal paraffins, 22% other saturates and 69% aromatics; it had an F–1–3 octane number of 95.4. The primary purpose was to determine the maximum charge which could be effectively separated over a given mass of the sorbent on a once-through basis and the minimum time required for the complete cycle of operations while maintaining an effective separation. By charging 10 g. of the preheated hydrocarbon mixture to a column of 150 g. of the sorbent, maintained at 450° C., in 15 seconds, followed by a 10 seconds' flush with nitrogen (methane worked equally as well) to ensure removal of non-normal hydrocarbons, then a further 30 seconds' sweep with nitrogen with recovery of essentially all of the normal hydrocarbons, followed by repetition of the cycle of operations over an extended period of time, the feed mixture was separated into an 80% by volume fraction having an F–1–3 octane rating of 100 and a 20% by volume fraction containing a high proportion of normal paraffins. The sweep gas was used at the rate of 2600 s.c.f./barrel of hydrocarbons. (S.c.f. designates cubic feet at standard conditions of temperature and pressure.) Thus, the mixture was separated at the rate of 600 g./hr. using 150 g. of sorbent, corresponding to a liquid hourly space velocity of about 3 volumes of hydrocarbons per volume (bulk volume) of sorbent per hour. This is a surprisingly high rate when it is considered that in commercial catalytic cracking operations the space velocity is of the order of only about 0.5 v./v./hr.

In another series of operations under similar conditions but with feed injection for 15 seconds with 0.01 s.c.f. of N_2, product sweep with 0.035 s.c.f. N_2 in 15 seconds, n-paraffin sweep with 0.2 s.c.f. N_2 in 60 seconds, at an average temperature of 450° C. at essentially atmospheric pressure, for 50 cycles, the C_7–C_{10} commercial

reformate was separated into 84.5% product lean in n-paraffins with a refractive index of 1.4600 and an octane number, F–1–3, of 98.1 and 14.2% of n-paraffin-rich fraction having an index of refraction of 1.4256 (20/D).

Although the separations are advantageously effected in vapor phase at about one atmosphere pressure and at the temperatures specified, similar separations are obtained when the vapor mixture is subjected to an elevated pressure which may range up to 100 to 750 pounds per square inch or even higher up to 1000 p.s.i.g., particularly in the case of the lower boiling, gasoline range, hydrocarbons. When higher pressures are applied to the vapor mixture in contact with the sieve sorbent, the vapor concentration is higher and either more eluting gas or a longer time is required to remove the hydrocarbon from the solid. However, this is compensated for in part by the greater capacity of the solid for the normal hydrocarbons so that a greater amount of charge may be added to the solid mass before effluent non-straight-chain product is materially contaminated with normal hydrocarbons.

In general, in order to insure vapor phase separation, the temperature should be chosen so that the ratio of the absolute temperature in the contacting zone to the absolute boiling temperature of the highest boiling component of the mixture at the operating pressure is greater than unity and generally it is greater than 1.1, preferably at least 1.3. The temperature may be at any suitable level above 380° C., but below that of thermal cracking, under process conditions of flow and pressure, of the least stable hydrocarbon of the mixture, which is lower for more complex larger molecules than for the smaller normal paraffins. Also, the thermal stability of the solid sorbent must be considered, although this generally is not a primary limitation on the process. Although the process may be practiced at temperatures as high as about 600° C., operation at this temperature would generally require an elevated pressure for the separation of the light normal hydrocarbons, because of the reduced relative retention of the light normal hydrocarbons at this temperature. Consequently, it is generally preferred to operate at a temperature of up to about 550° C. and still more preferably up to about 500° C.

In processing a hydrocarbon fraction in accordance with this invention, a convenient method comprises: (1) establishing a bed of molecular sieve in a vessel, such as a tube or tower, which is suitably provided with heating means such as a jacket or internal coils; (2) passing feed through the bed while maintaining the desired bed temperature; (3) passing the effluent, which at first contains essentially only non-normal hydrocarbons to a product recovery means, which may be, for example, a condenser or an absorber with the usual associated equipment; (4) discontinuing flow of feed to the bed either (*a*) after a predetermined amount of feed (calculated to contain no more normal hydrocarbons than the sorbent mass has capacity to sorb) has been charged, or (*b*) when normal hydrocarbons to be separated first appear in the effluent from the sorbent bed; (5) passing sweeping gas through the bed to displace the non-normals; (6) continuing flow of sweeping gas, preferably at a higher flow rate, and passing the effluent to a separate recovery means to recover normal hydrocarbons; and (7) after the normal hydrocarbons have been removed from the bed, at least to the extent to which they are readily desorbed at the prevailing temperature and pressure, adding fresh feed to the sorbent charge and repeating the cycle. This procedure is readily modified to permit separate recovery of normal hydrocarbon fractions of different molecular weights, originally present in a relatively wide boiling feed fraction, by controlling the flow of effluent during the desorption step so that it is switched to a different recovery vessel as each progressively higher molecular weight cut of normal hydrocarbons appears in the effluent. Continuous analytical monitoring of the effluent, e.g. by a mass spectrometer, readily permits such controlled recovery.

In some cases, a small amount of normal hydrocarbons may result in the sorbent at the end of the desorption step in this process. This amount may vary with the temperature and other conditions used in the desorption step and with the molecular weight of the hydrocarbon. Sufficient normal hydrocarbon is desorbed so that at most only a small amount remains, which is very tenaciously held so that it does not appear to a substantial extent in the effluent during the step of recovering non-normals.

In the normal hydrocarbon removal step of this invention it is essential to have a substantial flow of an inert gas to sweep out the normal hydrocarbons. Helium, hydrogen, nitrogen and methane have been successfully used as such sweep gases. Other inert gases, i.e., gases which do not react with either the sorbent, the vessel or the reactants, are also suitable. For example, argon, flue gas (preferably scrubbed to remove reactive impurities), propane and other gases and vapors can be used as sweep gas.

As has been shown, it is not essential to use a sweep gas while the hydrocarbon feed is being charged. The feed may be added to the heated sorbent as a liquid, to be quickly vaporized by contact with sorbent, or it may be added as a vapor. If desired, sweep gas flow may be maintained through the sorbent mass at all times and the feed added as liquid or as vapor to the sweep gas. It will generally be preferred to maintain a relatively low rate of inert gas flow or no gas flow at all during the time when feed is added, and a substantial gas flow during the time when sorbed normal hydrocarbons are desorbed. The first sweep gas added after feed is discontinued serves to flush the remaining non-sorbed hydrocarbons out of the sorbent mass. The rate of gas flow during this flushing step may differ from that used during the sweeping step.

Referring to FIGS. 1, 2 and 3, it is readily seen that the process conditions can be selected either to separate essentially all of the normal hydrocarbons from the non-normal hydrocarbons, or they can be selected so that the lower normal hydrocarbons, e.g. up to n-hexane, can be separated with the non-normal hydrocarbons and separated from the higher normal hydrocarbons. This is particularly advantageous in the improvement of hydrocarbon fuels, such as gasoline, kerosene, and the like containing mixtures of hydrocarbons wherein the carbon number spread of the normal hydrocarbons is as high as 4 or 5, such as a platformate composed predominantly of C_6 to C_{10} hydrocarbons.

The mixtures which contain a wider range of normal hydrocarbons may be advantageously de-normalized by first separating the mixture, as by distillation, into two or more fractions of narrower ranges, and adding these successively to a column of the sorbent, the fraction of heaviest molecules first, in charge amounts selected so that the heavier normal hydrocarbons have traversed only a part of the column when the lightest fraction is added later and so that lightest and heaviest normal hydrocarbons reach the exit and essentially simultaneously. The addition of charge and eluting gas is then discontinued and the normal hydrocarbons are then swept out by means of a suitable sweep gas. By this means, the total time for separation and recovery of the higher normal hydrocarbons in a given column is used to greatest advantage to obtain further separation of other normal hydrocarbons.

The process of the present invention is useful in the separation of normal hydrocarbons from mixtures containing normals having a carbon number of at least 4 and generally at least 5. It is particularly suitable for mixtures containing normals from n-pentane or n-hexane through n-decane or n-dodecane and corresponding

olefins, but may be used with mixtures containing normals up to n-eicosane.

The foregoing illustrative separations demonstrate the utility of the present invention in a large scale process for the separation of mixtures of normal and non-normal hydrocarbons. It is particularly useful in upgrading gasoline hydrocarbon mixtures which contain normal paraffin hydrocarbons, whether they are straight-run fractions, thermally cracked fractions, catalytically cracked fractions or reformates. The normal paraffins in the gasoline boiling range have low octane values decreasing with increasing molecular weight, and their presence in gasoline reformates of various origins, whether from platinum catalyzed reforming, such as platforming, or from reforming with other catalysts, such as molybdenum oxide/alumina catalyst, is undesirable. However, their separation from the mixture usually is difficult and expensive, sometimes prohibitively so. By the present process, the normal paraffins are substantially completely removable from the gasoline boiling range fraction, or the process is readily adaptable to the removal of substantially all of the higher normal paraffins present while leaving a substantial portion to about all of the lower normal paraffins present in the non-normal-enriched product stream. The process also removes the normal olefins from the thermally and catalytically cracked products. Similarly, for the preparation of low freezing point highly paraffinic naphtha fractions to be used as, or for blending to, other hydrocarbon fuels, such as jet fuels and the like, fractions of the fuel or the entire blended fuel may be treated in accordance with the invention to remove the higher normal paraffins present, while removing or leaving the lower normal paraffins as desired, to lower the freezing or pour point of the fuel.

I claim as my invention:

A process for the separation and recovery of normal hydrocarbons and non-normal hydrocarbons from a plurality of mixtures of such hydrocarbons, said plurality consisting of separate and immediately successive narrow boiling fractions differing in boiling range and containing normal hydrocarbons of at least 5 carbon atoms per molecule which comprises maintaining a fixed bed columnar particulate mass of a solid zeolitic material having a rigid three-dimensional anionic network and having substantially uniform introcrystalline interstitial channels of from about 5 to about 6 Angstrom units diameter at a contacting temperature of from 380° C. to about 600° C.:

(1) passing the highest boiling of said fractions in vapor phase through said columnar mass to selectively retard the passage of the normal hydrocarbons through the mass while the non-straight-chain hydrocarbons pass through the mass,

(2) then passing said other fractions in vapor phase through said columnar mass separately and successively in order of decreasing boiling range, the fractions being charged in proportions selected so that the smallest and largest normal hydrocarbons begin to leave the columnar mass essentially simultaneously;

(3) discontinuing passage of said fractions to the mass before normal hydrocarbons begin to appear in substantial proportion in the effluent stream;

(4) passing an eluting gaseous material through the mass in the same direction as the said fractions to elute a substantial proportion of the retained hydrocarbons as a normal hydrocarbon-enriched stream; and

(5) repeating the cycle of steps (1), (2), (3) and (4).

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