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J. M. STUCKEY

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METHOD OF SEPARATING HYDROCARBONS

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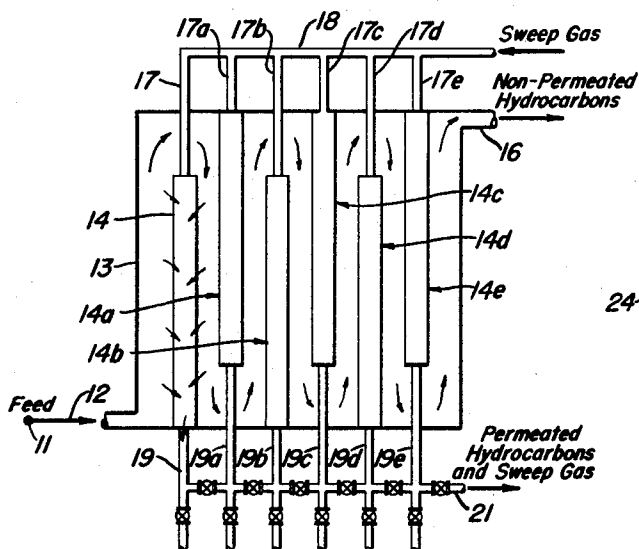


Fig. 1

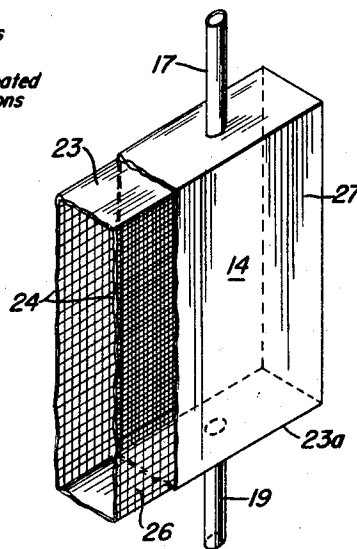


Fig. 2

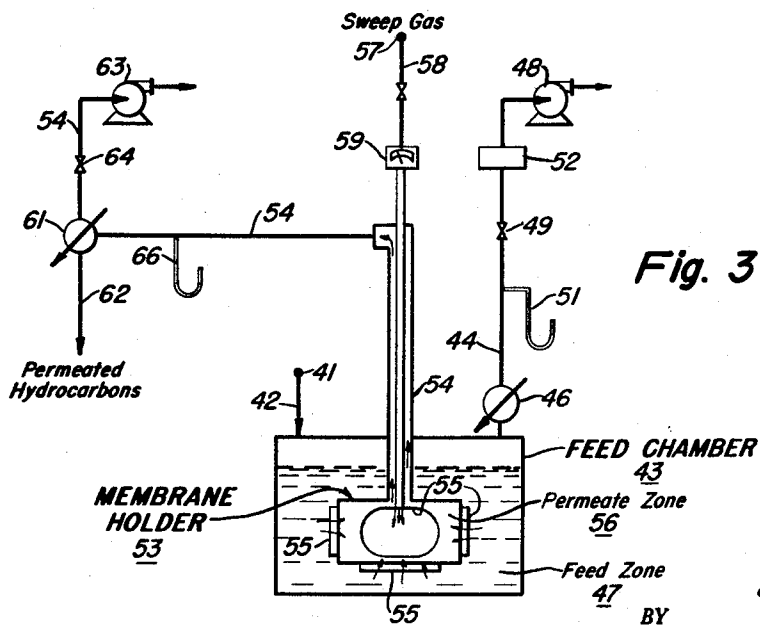


Fig. 3

INVENTOR.
James M. Stuckey

Joseph C. Kotarski
ATTORNEY

1

2,930,754

METHOD OF SEPARATING HYDROCARBONS

James M. Stuckey, Texas City, Tex., assignor to Pan American Refining Corporation, Texas City, Tex., a corporation of Texas, now by change of name to The American Oil Company

Application July 16, 1954, Serial No. 443,894

9 Claims. (Cl. 210—23)

This invention relates to the separation of certain hydrocarbons from mixtures thereof with other hydrocarbons by permeation through a non-porous membrane and it pertains more particularly to the use of an improved type of non-porous membrane.

It has heretofore been proposed that certain hydrocarbons be separated from hydrocarbon mixtures by permeation through membranes of rubber, chloroprene, neoprene, and the like, but the selectivities and/or permeation rates of such membranes were so low that the processes were commercially impracticable. An object of this invention is to provide a practical hydrocarbon permeation process of such improved selectivity and permeation rate that it can be employed on a commercial scale for separating mixtures of hydrocarbons according to type and/or boiling point. A more specific object is to provide a simple, inexpensive method and means for concentrating aromatics and/or olefins from gasoline boiling range hydrocarbon mixtures and/or to separate branched-chain paraffins such as isooctane from normal paraffins such as normal heptane in order that a naphtha fraction may be effectively separated into components of high octane number and low octane number, respectively. Other objects will become apparent in the course of the detailed description of the invention.

It has been discovered that hydrocarbon mixtures may be rapidly and effectively separated according to type, i.e. aromatic, unsaturated, saturated hydrocarbons, and/or molecular configuration and/or boiling point by causing a portion of the mixture to permeate through a non-porous membrane comprised of certain cellulose esters under defined conditions. For obtaining rapid selective permeation, a thin non-porous membrane is employed which is less than 10 mils and preferably 0.2 to 5 mils in thickness and comprised of cellulose esters containing acyl radicals of a type and in a quantity to permit certain of the hydrocarbons to dissolve in the membrane without rendering the membrane so soluble in the hydrocarbons as to rupture the permeation process. The carboxylic acid esters of cellulose which may be employed in making the membranes for use in this process are those which have at least a portion of introduced acyl groupings which contain more than 2 carbon atoms. Approximately 10% or more of the acyl radicals introduced into cellulose should have more than 2 carbon atoms. The cellulose esters preferably have from 2 to 4 carbon atoms in the introduced acyl grouping, although the number of carbon atoms may be more. Cellulose acetate is not effective for the selective permeation of hydrocarbons inasmuch as it is practically impermeable to hydrocarbons. However, cellulose acetate-butyrate is highly effective. Other examples of useful cellulose esters are cellulose propionate, cellulose acetate-propionate, cellulose butyrate, cellulose pentanoate, cellulose hexanoate, cellulose acetate-hexanoate, cellulose propionate-butyrate, cellulose benzoate, cellulose acetate-benzoate, and like compounds of single or mixed carboxylic acid esters of cellulose. The carboxylic acids employed in

2

esterifying cellulose may be straight-chain, branched-chain, or cyclic acids. In general, higher permeation rates of the hydrocarbons through the membrane are obtained when using cellulose esters having more than 2 carbon atoms in the introduced acyl grouping. If mixed esters of cellulose such as cellulose acetate-butyrate are employed, higher rates of permeation are obtained as the amount of butyryl groups is increased and the amount of acetyl groupings is decreased but the membrane is rendered more susceptible to rupture. When cellulose acetate-butyrate is used to make the membrane, the ratio of introduced butyryl to acetyl groups contained therein may vary between 99:1 to 10:90. However, when using cellulose ester membranes having introduced acyl groupings containing more than 2 carbon atoms, the different acyl groups may be contained therein in any ratio. As the number of carbon atoms in the introduced acyl grouping is increased, the membrane made therefrom is somewhat less stable under permeation conditions and more susceptible to rupture. If desired, the cellulose molecules may also contain some introduced ether groupings. The separation of hydrocarbons from a mixture of hydrocarbons by selective permeation through a non-porous membrane comprised of certain cellulose ethers is described and claimed in copending application Serial No. 443,893, filed on even date herewith.

The cellulose molecule consists of recurring units each of which contains 3 hydroxyl groups and which have the chemical formula $C_6H_{10}O_5$. A sufficient number of the hydroxyl groups should be esterified so that the resulting cellulose ester will dissolve at least certain of the hydrocarbons in the mixture to be separated. It is preferred to employ a cellulose ester which contains some unreacted hydroxyl groups because such cellulose esters are less susceptible to softening or solution of the membrane by the hydrocarbons to the extent that the film is ruptured during the permeation process. Most commercial cellulose esters have between 2.2 to 2.6 of the 3 hydroxyl groups contained in each unit of the cellulose molecule in the esterified condition. However, effective membranes may be prepared from cellulose esters which have a higher or lower degree of esterification, although the membranes are preferably prepared from cellulose esters having some free or non-esterified hydroxyl groups. Ordinarily, from about 1.8 to 2.8 of the 3 hydroxyl groups contained in the cellulose molecule may be esterified. The degree of esterification is usually expressed in terms of percent by weight of the particular acyl group contained in the cellulose.

The membrane employed is non-porous, i.e. free from holes and other defects which destroy a continuous surface. If the membrane has pinholes or the like which allows hydrocarbons to leak through, the selectivity of the permeation process is reduced or eliminated. The membrane may also be formed from physical mixtures of different cellulose esters or physical mixtures of cellulose esters and cellulose ethers. The membranes may be formed by conventional techniques such as extrusion or by casting from a solution of the cellulose ester in a solvent system. Although any of a number of solvent systems known to the art may be used, they are not all precisely equivalent inasmuch as membranes cast from various systems may have varying degrees of permeability to the permeating hydrocarbons. A particularly effective solvent system is composed of methyl ethyl ketone, methyl isobutyl ketone, and acetone in a ratio of 3:3:5. Other ingredients such as antioxidants, stabilizers, plasticizers, and the like may be contained in the membrane to improve its strength, flexibility, physical stability, to increase the rate of permeation and/or selectivity, or for other purposes, provided that the composition of

such ingredients and the amounts in which they are employed and are not such as to render the membrane impermeable to hydrocarbons and/or eliminate the selectivity of the membrane. Supports such as fine mesh wire screen or the like may be used as backing materials to minimize the chances of rupturing the membrane.

The invention has broad application to the separation of mixtures of hydrocarbons into fractions having different concentrations of the component hydrocarbons than were contained in the original mixture. Hydrocarbon mixtures can be separated into fractions having differing concentrations of hydrocarbons of a particular type, i.e. aromatics, unsaturated, and saturated hydrocarbons. The various types of hydrocarbons permeate more rapidly through the membrane in the following order: saturated hydrocarbons, unsaturated hydrocarbons, aromatic hydrocarbons. This separation of hydrocarbons by type can be accomplished to a striking degree when narrow boiling hydrocarbon mixtures are employed as the feed mixture. The process of this invention is also capable of separating hydrocarbon mixtures into fractions according to the structural configuration of the hydrocarbon molecules present in the feed hydrocarbon mixture. Thus hydrocarbons can be separated according to their molecular configuration into cyclic-, branched-chain, and straight-chain hydrocarbons, the particular configuration permeating more rapidly through the membrane in the order listed when the hydrocarbons have the same number of carbon atoms. Branched-chain hydrocarbons may be separated into fractions having a low degree of branching and fractions having a higher degree of branching, the former permeating more rapidly. Separation according to molecular configuration is particularly effective when the hydrocarbons are of the same type such as either olefins or paraffins. A separation can also be made between hydrocarbons based upon their molecular weights, the lower molecular weight hydrocarbon permeating through the membrane more rapidly than the higher molecular weight hydrocarbon. The separation of hydrocarbons according to molecular weight is preferably accomplished when using hydrocarbons of the same type and molecular configuration, e.g. cyclohexane from methylcyclohexane. Lower boiling hydrocarbons tend to permeate the membrane more rapidly than higher boiling hydrocarbons. The separations discussed supra are most advantageously performed using a narrow boiling mixture, e.g. boiling within about 20–30° C., although wider boiling mixtures of hydrocarbons may be employed. An especially preferred hydrocarbon mixture boils within the gasoline boiling range and has a boiling range of about 15° C.

Examples of suitable mixtures of hydrocarbons are natural or refined mineral oils. For example, a petroleum distillate such as gasoline may be separated into a permeate having a higher octane number than the original gasoline and higher than the non-permeated portion of gasoline. Among the gasoline components which may be so treated are naphtha fractions such as virgin naphtha, naphtha obtained from thermal cracking or from catalytic conversion processes such as catalytic cracking, catalytic hydroforming, and the like. Charging stocks to various petroleum conversion processes may be treated to remove undesirable components, e.g. a cycle oil from the cracking of gas oil may be processed in accord with this invention to remove as a permeate certain materials which increase the rate of coke deposition on catalysts when the cycle oil is catalytically cracked to produce further amounts of gasoline. Preferred charging stocks to the process of this invention are those boiling within the gasoline boiling range. Normally liquid fractions which boil within this range are suitable charging stocks for segregation into a permeate fraction enriched in aromatics and olefins and a non-permeated fraction having a higher concentration of paraffinic hydrocarbons. Narrow

boiling fractions such as a mixture of benzene or toluene with isooctane can be separated into a permeate fraction having a concentration of the aromatic hydrocarbon greater than that contained in the non-permeated hydrocarbons or in the initial mixture. A mixture of olefins and paraffins such as hexene or heptene with hexane or heptane may be separated into a permeate fraction having a higher concentration of olefins than is contained in the non-permeated fraction. Likewise, cyclohexane may be separated from a cyclohexane. Straight-chain paraffins may be separated from branched-chain paraffins or from cycloparaffins in this same fashion. Diolefins such as butadiene or isoprene can be obtained in concentrated form in the permeate from a mixture with olefins and/or paraffins. Butane can also be concentrated in the permeate from mixtures thereof with pentane or hexane.

The permeation process is carried out by contacting one side of the membrane with the hydrocarbon mixture which may be in the liquid or vapor state and removing permeated hydrocarbons from the opposite side of the membrane in either the liquid or vapor state. The hydrocarbon mixture may be continuously introduced into the charging zone so that it contacts one side of the membrane and non-permeated hydrocarbons may be continuously removed from this zone after having contacted the membrane. Permeated hydrocarbons may be continuously withdrawn from the permeate zone. It is believed that permeation occurs because the concentration of permeating hydrocarbons at the surface of the membrane on the permeate side is less than the concentration of the permeating hydrocarbons at the surface of the membrane in the charging zone. Thus, the permeated hydrocarbons should be rapidly removed from the surface of the membrane in the permeate zone to insure rapid permeation of the hydrocarbons. This may be accomplished by removing permeated hydrocarbons from the surface of the membrane on the permeate side or by diluting permeated hydrocarbons in this zone with a diluent or sweep gas or liquid, for example, steam, air, and the like. When liquid-liquid systems are employed on opposite sides of the membrane, a diluent or sweep liquid is circulated about the permeate surface of the membrane. When permeate hydrocarbons are obtained in the permeate zone in the vapor state, the permeate hydrocarbons may be removed from the permeate zone by employing a lower pressure than exists on the charging side or by using a sweep gas to dilute and/or remove the permeated hydrocarbons. When the hydrocarbons in both the charging zone and the permeate zone are in the vapor phase, a pressure differential is employed to facilitate the permeation of the hydrocarbons. Pressure differentials of from 10 mm. Hg to as high as 100 p.s.i.g., dependent upon the strength of the membrane and the effectiveness of the manner in which it is supported, may be used. Under such operating conditions, the pressure may be super-atmospheric, atmospheric, or sub-atmospheric, dependent upon the pressure differential existing between the two zones. It is preferred to operate the permeate zone at sub-atmospheric pressures so that the permeated hydrocarbons when removed in the vapor state are easily evaporated. The preferred mode of operating the permeation process consists of contacting the feed mixture of hydrocarbons while in the liquid state with the membrane and removing the permeate in the form of a vapor from the permeate zone. This permeate may be removed by employing a reduced pressure in the permeate zone or by sweeping the vapors of the hydrocarbons with a gas such as air. It has been found that when operating the permeation process in this preferred manner it is possible to obtain increased rates of permeation of about 40% higher than those obtainable by having the hydrocarbons in the vapor state on both sides of the membrane. If desired, it is possible to operate with the pressure differential maintained across the membrane to insure

rapid permeation of the hydrocarbons and also to use a sweep gas or liquid, whichever is called for by the conditions, to increase the permeation rate.

While the invention is not to be limited by the following theory, it is believed that the permeation of hydrocarbons through the membrane consists of three stages: (1) solution of the hydrocarbons in one side of the membrane, (2) permeation of the hydrocarbons through the membrane, and (3) removal of the hydrocarbons from the opposite side of the membrane. The selectivity which the membrane exhibits toward the hydrocarbons undergoing permeation is believed to be determined in the first stage, since there is no appreciable change in selectivity with a variation in thickness of the membrane. The rate of permeation of the hydrocarbons varies inversely with the thickness of the membrane, but if the membrane is thicker than about 10 mils the permeation rate is reduced to an almost negligible level. To obtain the highest rates of permeation of the hydrocarbons it is preferred to employ the thinnest membrane possible which has the necessary strength to avoid rupturing under the conditions of pressure differential, temperature etc., used in the permeation process. It should be less than about 5 to 10 mils and may be as thin as about 0.5 mil or less. Supports such as fine mesh wire screen, porous sintered metals or ceramic materials may be used as backing or supporting materials to assist in minimizing the chances of rupturing the membrane while yet employing as thin a membrane as possible.

The rate of permeation of hydrocarbons through the membrane varies directly with the temperature. An increase in the operating temperature of about 10° C. will increase the rate of permeation of the hydrocarbons through the membrane by as much as 100%. The effect of temperature on the rate of permeation of individual hydrocarbons is not necessarily the same, and it may vary for various hydrocarbons. It may generally be said that an increase in the operating temperature of the permeation process will increase the rate of permeation with little or no effect on the selectivity of the membrane for the various hydrocarbons. However, as the operating temperature is increased there is an increase in the tendency of the membrane to soften to the point of rupture or dissolve. The permeation process is preferably operated at as high a temperature as possible to obtain maximum permeation rates without causing the membrane to soften to the point of rupture or dissolve. The permeation process may be operated at a temperature of from about 0° C. to about 150° C., preferably between about 50° C. to 120° C.

The type of hydrocarbons and the relative concentration in which certain types of hydrocarbons contact the membrane, the operating temperature of the permeation process, and the composition of the membrane affect the stability of the membrane during the permeation process, i.e. the likelihood of softening of the membrane to the point of rupture or dissolving of the membrane. Aromatic hydrocarbons such as benzene, toluene, dimethyl naphthalenes, and the like and to a lesser extent the unsaturated hydrocarbons, tend to cause the membrane to soften. This effect is more pronounced as their concentration in the hydrocarbon mixture is increased, especially in regard to their concentrations in liquid feed hydrocarbon mixtures to the permeation process. When hydrocarbons are obtained in the permeate zone in the vapor phase, the concentration of the aromatic and/or unsaturated hydrocarbons is of much lesser importance since they are rapidly carried away from the surface of the membrane. As was pointed out previously, increasing the operating temperature of the permeation process increases the possibility of the membrane softening to the point of rupture. The composition of the membrane itself will affect the maximum temperature at which the permeation process can be operated and the concentration of aromatic and unsaturated hydrocarbons which

can be tolerated without softening of the membrane to the point of rupture. As more acyl groups are introduced into the cellulose molecule (with a consequent decrease in the number or concentration of free or unaltered hydroxyl groups) there is an increased tendency for the cellulose ester membrane to soften to the point of rupture. The greater the number of carbon atoms in the introduced acyl group, the greater is this tendency. For example, a membrane made from cellulose acetate-butyrate having an acetyl content of about 13% and a butyryl content of 38% by weight will soften to about the point of rupture if the concentration of toluene in a feed mixture of toluene-n-heptane is more than about 80% by volume when operating at a temperature of 90° C., and when the concentration of toluene is more than about 90% it will soften to about the point of rupture when operating at a temperature of 70° C. When the feed mixture is dimethylnaphthalene approximately the same concentrations and temperatures apply. If using a membrane made from cellulose acetate-butyrate having an acetyl content of 7% and a butyryl content of 48%, the membrane will soften to about the point of rupture at 90° C. when using a feed mixture containing more than about 40% toluene in n-heptane, and it will soften to about the point of rupture at 50° C. when using a feed mixture containing more than about 60% toluene in n-heptane.

The rate of selective permeation of hydrocarbon mixtures, such as mixtures of paraffinic hydrocarbons of differing molecular configuration, through non-porous membranes may be increased by contacting the membrane during the permeation process with an added aromatic and/or unsaturated hydrocarbon. This method has applicability which is broad to those membranes which permit hydrocarbons to permeate selectively therethrough. This subject matter is claimed in copending application Serial No. 465,495.

The rate of selective permeation of hydrocarbons through non-porous membranes can be increased manyfold by contacting the membrane during permeation with a non-hydrocarbon solvent material, e.g. oxygenated compounds such as alcohols, ethers, alcohol ethers, esters, ketones, acetals, and the like, and chlorinated compounds such as trichloroethylene, propylene chloride and the like. This method for increasing the rate of permeation has broad applicability to all membranes which permit certain hydrocarbons to permeate selectively. This subject matter is claimed in copending application Serial No. 465,497.

The permeation process may be operated as a batchwise or continuous operation. When operating continuously, the feed hydrocarbon mixture which is continuously introduced into the feed zone, contacts one side of the membrane and hydrocarbons which have not permeated through the membrane are then removed from the feed zone. The rate of introduction of the feed may be adjusted to provide the desired amount of non-permeated and permeated hydrocarbons. The permeated hydrocarbons are preferably continuously removed from the permeate zone. The permeated hydrocarbons or the non-permeated hydrocarbons may be further separated in subsequent permeation stages to obtain hydrocarbons in the desired concentration. It is of course essential that only a portion of the feed be allowed to permeate. The larger the portion permeating, the poorer is the degree of separation; whereas the smaller the portion which is allowed to permeate, the greater the degree of separation. The membrane may be used in the form of sheeting or tubing or in any form which preferably provides a maximum surface to volume ratio.

The invention will be more clearly understood from the following description and from the accompanying drawings.

Figure 1 is a diagrammatic drawing of an apparatus and process which illustrates a preferred embodiment

of the process of this invention for separating a catalytically cracked naphtha into a permeate fraction having a higher octane number than the feed naphtha and a non-permeated fraction having a lower octane number than the feed.

Figure 2 is an isometric view of one of the permeation cells shown in Figure 1.

Figure 3 is a diagrammatic representation of the apparatus employed in practicing the invention on a small scale.

Referring to Figure 1, the feed which consists of a catalytically cracked naphtha is passed at a temperature of 80° C. from source 11 by way of line 12 into permeation unit 13 which contains a battery of permeation cells 14, 14a, 14b, 14c, 14d, and 14e. It is introduced at a rate such that only a small fraction thereof is removed as non-permeated hydrocarbons. The liquid feed in permeation unit 13 is kept at about 80° C. The feed fills the unit and surrounds the individual cells. The feed travels a torturous path, passing upwardly along one side of a permeation cell and downwardly along the opposite side of the cell and so forth until only a small fraction of the original feed, which now consists of non-permeated hydrocarbons, is removed by way of line 16 from the permeation unit 13. Each permeation cell, which consists of a box-like apparatus wherein the outer surface comprises a non-porous membrane of cellulose acetate-butyrate having an acetyl content of about 7% and a butyryl content of about 48% and being about 0.2 mil in thickness, is attached to the inside walls of permeation unit 13. The supporting means for the membrane, which will be more fully described in connection with Figure 2, is contained in the permeation cell to prevent rupturing of the membrane during the process of permeation. The permeation cells 14, 14a, 14b etc., are attached at the bottom and top to the walls of permeation unit 13 with a space provided either above or below the respective cells to provide a torturous path for the feed naphtha. Such a pathway is desired to obtain a great amount of contact time of the feed with the membrane per volume of permeation unit, and to prevent localized differences in concentration of the components of the feed at different places on the membrane. Each permeation cell 14, 14a, 14b, 14c, 14d and 14e is provided at its top with an inlet 17, 17a, 17b, 17c, 17d and 17e respectively, which in turn is connected to header 18. A sweep material, herein air, is passed into header 18 and thence by way of lines 17, 17a, 17b, 17c, 17d, and 17e into permeation cells 14, 14a, 14b, 14c, 14d, and 14e respectively, to sweep the permeated hydrocarbons from the inner surface of the cellulose acetate-butyrate membrane. The use of a sweep material is not essential, but it is preferred to employ it in order to increase the rate of permeation of the hydrocarbons through the membrane. The permeating hydrocarbons within the permeation cells 14, 14a, etc., are maintained in the vapor phase by maintaining a low absolute pressure, herein 30 mm. Hg absolute, in the inside or permeate zone of the permeation cells. An absolute pressure of slightly higher than atmospheric is maintained on the feed side of the membrane. The mixture of permeated hydrocarbon vapors and air sweep gas is removed from each permeation cell 14, 14a, 14b, 14c, 14d, and 14e by way of lines 19, 19a, 19b, 19c, 19d, and 19e respectively. The hydrocarbons contained in the mixtures withdrawn from each permeation cell may be separately condensed and recovered or passed into header 21 and combined, and then passed to condenser not shown wherein the permeated hydrocarbon vapors are condensed and recovered from their gaseous mixture with air. The low absolute pressure or vacuum is maintained within permeation cells 14, 14a, 14b etc., by vacuum pumps not shown but attached to lines 19, 19a, 19b etc., respectively and/or to header 21. The pumps also serve to withdraw permeated hydro-

drocarbons and the sweep gas air from the permeation cells and pass the mixture to the condensers where the permeated hydrocarbons are recovered. The permeated hydrocarbons withdrawn from permeation cell 14 have a higher octane number than the feed hydrocarbons, a higher octane number than the non-permeated hydrocarbons, and may also have a higher octane number than the permeated hydrocarbons withdrawn from permeation cell 14a. The permeated hydrocarbons withdrawn from permeation cell 14a in turn may have a higher octane number than the permeated hydrocarbons withdrawn from permeation cell 14b and so forth, until permeated hydrocarbons which are withdrawn from permeation cell 14e may have a lower octane number than the feed hydrocarbon. The low octane fractions may thus be removed from the higher octane permeated fractions to provide a higher octane number gasoline fraction, or the high octane number permeated fractions may be used as blending components to increase the octane number of gasoline. If a still higher octane number naphtha is desired, the process may be repeated on the various permeated hydrocarbon fractions in a second, third or fourth stage.

Figure 2 is an enlarged isometric view of a partial cross section of permeation cell 14. It comprises two end plates 23 and 23a which are joined at corresponding corners with connecting means 24 to form a thin rectangular box-like framework. A very fine mesh wire screen 26 surrounds the framework and provides a supporting means for the cellulose acetate-butyrate membrane 27. Inlet pipe 17 for the sweep gas is attached to end plate 23 at the top of the permeation cell. Outlet pipe 19 for the permeated hydrocarbon vapors and the sweep gas air is attached to end plate 23a. The cellulose acetate-butyrate membrane covers the fine wire mesh supporting means 26 so as to provide a continuous surface of the membrane which is free of any cracks or openings.

Figure 3 diagrammatically represents a form of apparatus used in practicing the invention on a small scale. The hydrocarbon mixture feed is passed from source 41 by way of line 42 into feed chamber 43. Line 44 is connected through a condenser 46 to the top of chamber 43. Condenser 46 is employed in this line to condense any vaporized hydrocarbons which may tend to leave the feed zone 47, particularly when refluxing the feed hydrocarbons. Vacuum pump 48 is attached to line 44 to control the absolute pressure in feed zone 47 at any amount less than atmospheric. Needle valve 49 is contained in line 44 to assist in maintaining the desired absolute pressure in feed zone 47. The absolute pressure in line 44 and feed zone 47 is determined by manometer 51 attached to line 44. Any hydrocarbon vapors which escape condensation in condenser 46 are collected in trap 52. Membrane holder 53 is positioned within feed chamber 43 and has a box-type design with a circular opening in each of five of its faces. A threaded brass ring surrounds each opening and extends outwardly from the plane of the surface of the membrane holder to form a cylindrical extending threaded wall with a flat shoulder. A fine mesh screen wire is supported and soldered across each opening and then the cellulose acetate-butyrate membrane is placed over each of the openings. A knurled brass ring fitting threaded on the inside is then used to seal the membrane to the shoulder of the cylindrical wall and thus seal the outer edge of the membrane with a screw type seal. A line 54 is attached to the top face of membrane holder 53 for the withdrawal of hydrocarbons which permeate from feed zone 47 through the membrane 55 into permeate zone 56. Sweep gas from source 57 is passed by way of valved line 58 through flowmeter 59 into permeate zone 56 to dilute the hydrocarbons contained therein and/or assist in removing them from the interior surface of the membrane. Permeated hydro-

carbons together with the sweep gas, if used, are removed in the vapor state from permeate zone 56 by means of line 54 and passed through an acetone-dry ice condenser 61 wherein permeated hydrocarbons are recovered and removed therefrom by way of line 62. The permeated hydrocarbons are removed from permeate zone 56 by maintaining a lower absolute pressure

were tested under approximately comparable conditions; were Cellulose AB-381 (a cellulose acetate-butyrate ester having a butyryl content of about 38% and an acetyl content of about 13%), Cellulose AB-500 (a cellulose acetate-butyrate ester having a butyryl content of about 48% and an acetyl content of about 7%), cellulose acetate having an acetyl content of about 40%, and a cellulose

Table I

Membrane	Run No.	Press. Diff., mm. Hg	Temp., °C.	Membrane Thickness in Mils	Vol. percent n-heptane in Permeate	Rate of Permeation, Gal./Hr./1,000 Sq. Ft. Membrane
Cellulose AB-381.....	1	730	100	1.5	86	1.0
Cellulose AB-500.....	2	600	94	1.75	89	4.2
Cellulose Acetate.....	3	730	110	5.0	(1)	(2)
Cellulose Nitrate.....	4	400	82	1.5	64	(2)

¹ Sample too small to analyze.

² Less than 0.1.

therein than is contained in feed zone 47. The absolute pressure is controlled in permeate zone 56 by a vacuum pump 63 in line 54. Needle valve 64 and manometer 66 are contained in line 54 to assist in regulating and measuring the absolute pressure contained therein and in permeate zone 56. The level of feed in feed zone 47 may be controlled so as to provide a vapor space between it and the membrane 55 contained in the membrane holder 53 or if desired, the feed may be contained in feed zone 47 so as to cover all surfaces of the membrane with liquid hydrocarbon feed. By regulating the pressure, the pressure differential, and temperature, it is possible to operate so that liquid hydrocarbons surround the membranes in the feed zone and vaporized hydrocarbons are withdrawn through the membrane into the permeate zone 56 and removed therefrom by means of line 54 and recovered from condenser 61.

The above described apparatus was employed in performing a number of experiments related to this invention. A series of experiments were performed wherein membranes prepared from different cellulose esters were used. In obtaining these data, a hydrocarbon mixture feed consisting of 50 volume percent of n-heptane and 50 volume percent isooctane was used. The permeation process was operated so that the hydrocarbons were in the liquid state in the feed zone and in the vapor state in the permeate zone. A pressure differential was maintained across the membrane, the permeate zone having the lower absolute pressure. The membranes, which

lose nitrate having a nitrogen content of about 12%. The above data show that cellulose nitrate and cellulose acetate membranes were practically impermeable to hydrocarbons, whereas the hydrocarbons permeate cellulose acetate-butyrate at a rapid rate. Because aromatic hydrocarbons generally permeate cellulose ester membranes more rapidly than paraffinic hydrocarbons, an experiment under approximately the same conditions as for run No. 3 was performed to determine whether toluene would permeate at a higher rate. The results indicated a rate of permeation approximately that observed in run No. 3.

A series of experiments were performed under approximately comparable conditions for separating hydrocarbons according to type and/or molecular configuration from very close boiling mixtures of hydrocarbons. In these runs the feed mixture of hydrocarbons was in contact in the liquid phase with a membrane of 1.5 mils thickness and consisting of Cellulose AB-500 (cellulose acetate-butyrate having an acetyl content of about 7% by weight and a butyryl content of about 48% by weight). The permeated hydrocarbons were removed in the vapor state from the surface of the membrane in the permeate zone by controlling the temperature and absolute pressure therein. The pressure within the membrane holder (permeate zone) was held at about 35 mm. Hg and the pressure within the feed zone adjusted to provide the desired pressure differential across the membrane. The data obtained in these runs are presented in Table II which follows.

Table II

Run No.	Feed Composition, Vol. Percent	Temp., °C.	Press. Diff., mm. Hg	Permeate Composition, Vol. Percent	Rate of Permeation, Gal./Hr./1,000 Sq. Ft. of Membrane	Separation Factor, α^1
5	50 n-Heptane.....	66	600	94 n-Heptane.....	0.7	16
6	50 Isooctane.....			89 n-Heptane.....		
7	50 n-Heptane.....	94	600	80 Methyl-cyclohexane.....	4.1	4
8	50 Isooctane.....			58 Heptene-2.....		
9	50 Methyl-cyclohexane.....	82	400	60 Hexene-1.....	7.3	1.5
10	50 Isooctane.....			35 Cyclohexene.....		
11	50 Heptene-2.....	52	400	52 Benzene.....	2.1	16
12	50 n-Hept.....			51 Benzene.....		
13	50 Hexene-1.....	52	400	37 Benzene.....	1.0	32
14	50 n-Hexane.....			4 Toluene.....		
15	20 Cyclohexene.....	69	400		3.4	20
16	80 Cyclohexane.....					
17	4.5 Benzene.....	82	400			
18	95.5 2,4-Dimethylpentane.....					
19	2.8 Benzene.....	69	400			
20	97.2 2,4-Dimethylpentane.....					
21	1.8 Benzene.....	82	400			
22	98.2 2,4-Dimethylpentane.....					
23	0.2 Toluene.....	69	400			
24	50 Isooctane.....					
25	49.8 Methylcyclohexane.....	82	400			
26						

$$^1 \text{ Separation Factor } \alpha = \frac{X_1 Y_2}{X_2 Y_1}$$

where X_1 and X_2 are concentrations of components 1 and 2 in the permeate and Y_1 and Y_2 are concentrations of components 1 and 2 in the feed.

The above data show that these cellulose ester membranes are very effective for separating very close boiling hydrocarbons into fractions according to type and/or structural configuration of the hydrocarbon molecules in the mixture. Runs 8 through 14 show that hydrocarbons can be separated by type and that the types permeate the membrane with increasing rates in the following order: saturated hydrocarbons, unsaturated hydrocarbons, and aromatic hydrocarbons. Aromatics were separated from other hydrocarbons. Unsaturated hydrocarbons such as olefins were separated from saturated hydrocarbons. The data also show that hydrocarbons can be separated according to the structural configuration of the molecules. Runs 5 through 7 indicate that hydrocarbons of about the same boiling point permeate the membrane at increasing rates in the following order of structural configuration: branched-chain, cyclic-chain, and straight-chain hydrocarbons. When permeating hydrocarbons having the same number of carbon atoms to separate them according to the structural configuration of their molecules, the hydrocarbons permeate at increasing rates in the order cyclic-chain, branched-chain, and straight-chain hydrocarbons. The separation factors obtained show the invention to be highly effective in separating hydrocarbons. Particularly outstanding is the separation which can be made between benzene and 2,4-dimethylpentane. If the octane number of the feed (82 CFR-Research) and the octane number of the permeate (98.4 CFR-Research) are calculated for run 11, the effectiveness of the invention in improving the octane number of petroleum distillates is readily apparent.

An additional series of experiments was performed under comparable conditions using a membrane consisting of Cellulose AB-381 (cellulose acetate-butyrate having a butyryl content of about 38% and an acetyl content of about 13%). In the experiments the feed mixture of hydrocarbons and the permeated hydrocarbons were both maintained in the vapor phase. A pressure differential was maintained across the membrane, the permeate zone having the lower pressure. The membrane was about one mil in thickness. The data obtained in these runs are presented in Table III which follows.

Table III

Run No.	Feed Composition, Vol. Percent	Temp., ° C.	Pressure Differential, mm. Hg	Permeate Composition, Vol. Percent	Rate of Permeation, Gal./Hr./1,000 Sq. Ft. of Membrane
15	50 Toluene.....	50	157	93 Toluene.....	28.8
	50 Isooctane.....				
16	50 Toluene.....	50	157	73 Toluene.....	29.8
	50 n-Heptane.....				
17	33.3 Toluene.....	57	151	80 Toluene.....	11.0
	33.3 n-Heptane.....			13 n-Heptane.....	
	33.3 Isooctane.....			7 Isooctane.....	

These runs are indicative of the high permeation rates which are obtainable when permeating a mixture containing an aromatic hydrocarbon through a cellulose acetate-butyrate membrane. It is also evident that the separation factor between aromatic hydrocarbons and the other hydrocarbons admixed therewith is quite high. Thus it may be seen that the process of this invention has particular applicability for the separation of aromatic hydrocarbons from mixtures thereof with non-aromatic hydrocarbons.

A number of runs were made under comparable conditions to determine whether the separation factor varies with a change in the composition of the feed hydrocarbon mixture. The feed was composed of n-heptane and isooctane in varying concentrations. A membrane about one mil in thickness and composed of Cellulose AB-500 (cellulose acetate-butyrate having butyryl content of about 48% and acetyl content of about 7%) was em-

ployed. The feed hydrocarbon mixture was maintained in the liquid phase and the permeated hydrocarbons were removed from the opposite side of the membrane in the vapor phase. The permeation process was operated at a temperature of 82° C. and a pressure differential of 400 mm. Hg across the membrane, the lower pressure being in the permeate zone. Butane was employed to sweep the vapors of the permeated hydrocarbons from the membrane. A butane flow of about 30 grams per hour was used. The results of the experiments are set forth below in Table IV which follows.

Table IV

Run No.	Feed Composition, Vol. Percent	Permeate Composition, Vol. Percent	Rate of Permeation, Gal./Hr./1,000 Sq. Ft. of Membrane	Separation Factor
19	10 n-Heptane.....	58 n-Heptane.....	0.5	12.4
	90 Isooctane.....			
20	30 n-Heptane.....	84 n-Heptane.....	1.0	12.3
	70 Isooctane.....			
21	50 n-Heptane.....	92 n-Heptane.....	1.6	11.5
	50 Isooctane.....			
22	70 n-Heptane.....	97 n-Heptane.....	2.0	13.9
	30 Isooctane.....			
23	90 n-Heptane.....	99+ n-Heptane..	2.6	11.4
	10 Isooctane.....			

Although the concentration of n-heptane in the feed mixture of n-heptane and isooctane varied from 10 to 90%, the separation factor remained approximately constant at about 12.

To demonstrate the effectiveness of the process of this invention for separating a mixture of branched-chain paraffins, an experiment was performed employing as the hydrocarbon feed a mixture of 50 volume percent of 3-methylpentane with 50 volume percent of 2,3-dimethylpentane. This was partly permeated through a Cellulose AB-500 membrane (cellulose acetate-butyrate having a butyryl content of about 48% and an acetyl content of about 7%) and being 1.8 mils in thickness. The hydrocarbon mixture feed was contacted in the liquid phase with the membrane and the permeated hydrocarbons were removed from the opposite side of the membrane in the vapor phase. The permeation process was operated at

62° C. and 730 mm. Hg pressure differential was maintained across the membrane. A butane sweep gas was employed at a rate of approximately 30 grams of butane per hour. The results obtained are shown in run 24 below.

Run No.	Feed Composition, Vol. Percent	Permeate Composition, Vol. Percent	Rate of Permeation, Gal./Hr./1,000 Sq. Ft. of Surface
24	50 3-methylpentane.....	50 3-methylpentane..	5.3
	50 2,3-dimethylpentane..		

This run illustrates that a separation can be made so as to concentrate branched-chain paraffins having a low degree of branching in the permeate from mixtures there-

of with branched-chain paraffins having a higher degree of branching, the latter tending to concentrate in the non-permeated hydrocarbon mixture.

The results of a number of selected comparative and representative experiments are set forth below in Table V. In these runs, changes were made in operating variables which affect the permeation process to indicate their magnitude as operating factors when practicing this invention. The effect of maintaining the feed hydrocarbons in the liquid or vapor phase, the influence of temperature, and the effect of changes in the pressure differential were determined in these runs. In all the experiments a Cellulose AB-500 membrane (cellulose acetate-butyrate having a butyryl content of about 48% and an acetyl content of about 7%) was used. The membrane was 2.0 mils in thickness. In each run, the permeated hydrocarbons were withdrawn in the vapor phase from the permeate zone. A butane sweep gas was used at a flow rate of 30 grams per hour in runs 25 and 26 to remove and/or dilute permeated hydrocarbons from the membrane surface.

Table V

Run No.	State of Feed	Feed Composition, Vol. Percent	Temp., ° C.	Press. Diff., mm. Hg	Permeate Composition, Vol. Percent	Rate of Permeation, Gal./Hr./1,000 Sq. Ft. of Membrane
25-----	Liquid	50 Methylcyclohexane... 50 Isooctane.....	83	405	80 Methylcyclohexane...	3.3
26-----	Vapor	50 Methylcyclohexane... 50 Isooctane.....	83	405	do-----	2.4
27-----	Liquid	50 n-Heptane..... 50 Isooctane.....	66	600	95 n-Heptane.....	0.7
28-----	do	50 n-Heptane..... 50 Isooctane.....	94	600	89 n-Heptane.....	4.1
29-----	do	50 n-Heptane..... 50 Isooctane.....	66	200	96 n-Heptane.....	0.50
30-----	do	50 n-Heptane..... 50 Isooctane.....	66	400	do-----	0.65
31-----	do	50 n-Heptane..... 50 Isooctane.....	66	730	95 n-Heptane.....	0.70

It will be noted from runs 25 and 26 that a rate of hydrocarbon permeation of approximately 50% higher was obtained when liquid hydrocarbon feed rather than vapors of the feed contacted the membrane. This operating factor did not affect the selectivity or separation factor. Runs 27 and 28 indicate that increasing the temperature of operation increases the rate of hydrocarbon permeation and diminishes somewhat the selectivity of the process for particular hydrocarbons. Runs 29, 30, and 31 show that an increase in pressure differential will increase the rate of hydrocarbon permeation with little if any effect on the selectivity of the process for individual hydrocarbons.

Thus having described the invention what is claimed is:

1. A process which comprises contacting a charge liquid hydrocarbon mixture with one side of a thin plastic membrane which is free from holes, which has a thickness of about .2 to 5 mils, and which is comprised of a carboxylic acid ester of cellulose in which an average of from about 1.8 to 2.8 of the three hydroxyl groups contained per cellulose molecule have been esterified, the ester groups containing between 2 and 6 carbon atoms per ester group and at least 10% of the ester groups having more than 2 carbon atoms per ester group, permeating a portion of the liquid mixture in contact with said membrane through said membrane, and removing from the opposite side of said membrane a vaporized permeated portion having a composition different from said charge liquid hydrocarbon mixture.

2. The process of claim 1 wherein the charge liquid

hydrocarbon mixture comprises a mixture of at least two hydrocarbons of differing type selected from the types of hydrocarbons consisting of aromatic hydrocarbons, unsaturated hydrocarbons, and saturated hydrocarbons.

3. The process of claim 1 wherein the charge hydrocarbon mixture boils within the gasoline boiling range.

4. The process of claim 3 wherein the charge hydrocarbon mixture contains a substantial amount of aromatic hydrocarbons and the permeated portion contains a higher concentration of aromatic hydrocarbons than is present in the charge liquid hydrocarbon mixture.

5. The process of claim 1 wherein the charge hydrocarbon mixture is a petroleum distillate.

6. The process of claim 1 wherein the charge hydrocarbon mixture is a narrow boiling range mixture whose components boil within a range of 30° C. of each other.

7. The process of claim 1 wherein the cellulose ester is cellulose propionate.

8. The process of claim 1 wherein the cellulose ester is cellulose butyrate.

9. The process of claim 1 wherein the cellulose ester

is cellulose acetate-butyrate having an acetyl content of 7 to 15% by weight and a butyryl content of 30 to 50% by weight.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,930,754

March 29, 1960

James M. Stuckey

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

Column 1, line 30, before "boiling" insert -- molecular configuration and/or --; column 3, line 2, for "and are not such" read -- are not such --; column 10, Table II, last column thereof, under the heading "Separation Factor, α^1 ", seventh line, for "16" read -- 26 --.

Signed and sealed this 8th day of November 1960.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON

Commissioner of Patents