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2,880,254

## DESOXYCHOLIC ACID AS A SEPARATING AGENT

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No Drawing. Application October 4, 1956  
Serial No. 613,806

10 Claims. (Cl. 260—676)

This invention relates to a process for resolving hydrocarbon mixtures comprising components of relatively straight chain structure by contacting the mixture in an adsorptive-type separation procedure with desoxycholic acid. More specifically, this invention concerns a process for separating relatively straight chain aliphatic hydrocarbons from mixtures of the same with relatively more branched chain and cyclic hydrocarbons by a method which comprises contacting the hydrocarbon mixture with discrete particles of desoxycholic acid and thereafter withdrawing as a raffinate stream the components of the hydrocarbon mixture having relatively branched chain and cyclic structure.

One embodiment of the present invention relates to a process for separating an aliphatic hydrocarbon of relatively lesser branched chain structure than other components of a mixture of hydrocarbons from said other hydrocarbon components which comprises contacting said mixture with desoxycholic acid and thereafter separating a fraction enriched with respect to at least one of said other hydrocarbon components.

A more specific embodiment of this invention concerns a method for separating a normal paraffin containing from 5 to about 20 carbon atoms per molecule from branched chain paraffinic and cyclic hydrocarbons which comprises introducing a hydrocarbon mixture comprising said normal paraffin and a hydrocarbon component selected from said branched chain and cyclic hydrocarbons into contact with desoxycholic acid at a temperature of from about 0° to about 120° C. and at sufficient pressure to maintain the hydrocarbon mixture in substantially liquid phase and thereafter recovering a raffinate comprising a hydrocarbon selected from said branched chain paraffinic and said cyclic hydrocarbons from a desoxycholic acid complex of said normal paraffin and recovering the normal paraffin from said complex by contacting the complex with n-pentane at the aforementioned temperature and pressure conditions.

The present process for separating hydrocarbon mixtures is dependent upon the selective action of a specific organic compound, that is, desoxycholic acid, in selectively combining with aliphatic hydrocarbons of relatively straight chain configuration to form what is believed to be an adduct or complex between the acid and the hydrocarbon, although the present process is not intended to be necessarily limited in its scope to such explanation of the activity of the desoxycholic acid as a separating agent. In any event the net effect of contacting the desoxycholic acid with a hydrocarbon mixture containing relatively straight chain aliphatic components as well as branched chain and/or cyclic components is the selective retention of the relatively straight chain hydrocarbons and the rejection into a raffinate phase of the branched chain and/or cyclic hydrocarbons contained in the mixture.

Suitable hydrocarbon feed stock mixtures utilizable in the present separation process include any hydrocarbon

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mixture containing normal or relatively straight chain aliphatic components of paraffinic, olefinic or diolefinic structure in admixture with one or more members of the group comprising the aliphatic hydrocarbons of more highly branched chain structure than the component to be separated, naphthenic hydrocarbons or aromatic hydrocarbons of mono- or bicyclic ring structure. A particularly useful application of the process is in the treatment of gasoline boiling range fractions for the purpose of increasing the octane number of the fraction by removing the relatively non-branched chain aliphatic hydrocarbons which have the lowest octane rating of the various classes of hydrocarbons and which reduce the octane rating of gasoline boiling range fractions in which these hydrocarbons occur. Thus, by subjecting a mixture of hydrocarbons boiling in the gasoline range to treatment with the present separating agent, the effluent from the process contains a relatively greater proportion of the more highly octane rated isoparaffinic and cyclic hydrocarbons than the feed stock mixture because of the selective removal of the normal or relatively straight chain aliphatic components from the mixture. The hydrocarbons thus removed from the gasoline fraction by the present separating agent may be separately recovered and subjected to a suitable conversion process, such as an isomerization or a reforming process to convert the relatively straight chain hydrocarbons thus recovered into branched chain or cyclic isomers of higher octane number. The process, in general, is applicable to hydrocarbon fractions containing components having at least 4 carbon atoms per molecule, preferably hydrocarbon mixtures of C<sub>5</sub> to C<sub>12</sub> composition. When a charging stock comprising high molecular weight hydrocarbons (which are generally quite viscous at the process operating temperatures) is utilized in the process, it is preferably diluted with a C<sub>5</sub>, C<sub>6</sub> and/or C<sub>7</sub> branched chain or cyclic hydrocarbon diluent in order to reduce the viscosity of the charge stock.

A convenient method of operating a contacting type of separation process, suitable for use with the present reagent, comprises mixing the desoxycholic acid separating agent with the hydrocarbon mixture in liquid phase and thereafter filtering the resulting mixture to recover the separating agent containing adsorbed or occluded thereon the normal or straight chain aliphatic hydrocarbon components of the mixture. Since the present desoxycholic acid separating agent is substantially insoluble in the hydrocarbon feed stock mixture, another means of operating such a separation process comprises passing the hydrocarbon feed stock through a column packed with discrete particles of the desoxycholic acid until the latter has adsorbed sufficient normal or straight chain aliphatic hydrocarbons to substantially saturate the capacity of the separating agent to adsorb additional hydrocarbon. In this type of separation the desoxycholic acid separating agent may be composited with or deposited on a suitable solid supporting material, such as charcoal, sand, quartz chips, brick, Beryl saddles or other solid, generally porous material, insoluble in the hydrocarbon stream. The latter adsorption type procedure may be effected under liquid-solid phase conditions or gas-solid phase conditions, depending upon the temperature of the feed stock and the ambient pressure. In either method, the temperature of operation must be such that the separating agent is maintained in the apparatus in substantially solid phase, that is, at a temperature below the melting point of the normally solid desoxycholic acid. At atmospheric pressures, the contacting temperature is preferably maintained within the range of from about 20° to about 120° C. although higher or lower temperatures are also feasible. For

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most hydrocarbon mixtures, however, temperatures in the above-indicated range and pressures in the region of atmospheric pressure are suitable for effecting the separation. In a gas-solid phase type of separation, the feed mixture in gaseous phase is introduced into the apparatus containing the desoxycholic acid as a stationary, packed bed (the so-called "fixed bed" technique) or the velocity of the gas phase may be sufficient to continuously suspend the desoxycholic acid in the hydrocarbon gaseous phase (the so-called "fluidized bed" technique). In many moving bed procedures, either the fluidized or compact moving bed methods, countercurrent flow arrangements may be effected by charging the fresh feed stock into one end of the apparatus and charging fresh or regenerated adsorbent into the other end. The spent adsorbent containing the relatively straight chain components of the mixture adsorbed on the desoxycholic acid is removed from the end of the apparatus into which the fresh feed is introduced. Still another effective method of separation comprises mixing the hydrocarbon feed stock with an aqueous slurry of desoxycholic acid in finely divided condition and thereafter allowing the resulting phase separation to take place, the normal or relatively straight chain hydrocarbon components of the feed stock entering into combination with the desoxycholic acid to form a water-insoluble, solid phase component of the slurry, while the relatively branched chain or cyclic hydrocarbon components of the feed stock form a separate, liquid phase which may be decanted or centrifuged from the slurry. Instead of utilizing water as the suspending medium for the slurry, a hydrocarbon having a boiling point above or below the feed stock mixture may be substituted for the water to provide the fluid phase, the non-adsorbed, branched chain or cyclic hydrocarbon components of the feed stock mixing with an excess of the liquid hydrocarbon to form an effluent raffinate phase which may be distilled or otherwise treated to separate the added hydrocarbon utilized as suspending medium from the non-adsorbed components of the feed stock mixture. The preferred hydrocarbons for this purpose are the cyclic and branched chain hydrocarbons of lower molecular weight (therefore, of lower boiling point) than the components of the feed stock mixture. Typical hydrocarbons of the latter type include isobutane, isopentane, 2,3-dimethylbutane, cyclohexane and its methyl- or ethyl-substituted homologs, or other relatively low molecular weight hydrocarbons of the class not adsorbed by the present separating agent.

The desoxycholic acid-hydrocarbon adduct or complex formed by adsorption of the normal or relatively straight chain hydrocarbon component of the feed stock on the desoxycholic acid during the separation process may be individually treated following the separation process in order to recover the adsorbed hydrocarbon, if desired. For this purpose, the adduct or complex may be heated above the boiling point of the adsorbed hydrocarbon to remove the adsorbed hydrocarbon by distillation from the generally higher boiling desoxycholic acid; such vaporization preferably being effected under reduced pressure in order to increase the quantity and rate of recovery of the adsorbed hydrocarbon. Another suitable method for recovering the adsorbed hydrocarbon comprises washing the adduct or complex with an excess of a liquid or gaseous hydrocarbon containing or comprising relatively straight chain hydrocarbons which are preferably adsorbed by the desoxycholic acid separating agent and thereafter distilling the resulting hydrocarbon effluent to recover the wash hydrocarbon separate from the desorbed hydrocarbon. In the latter method of recovery it is generally preferred to utilize a hydrocarbon washing agent which boils above or below the boiling point of the adsorbed hydrocarbon (for example, n-pentane, n-hexane or other relatively straight chain hydrocarbon) in order to facilitate separation of the desorbed hydrocarbon from the excess desorbing hydro-

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carbon in the wash effluent. This recovery operation is preferably effected under countercurrent flow conditions in order to substantially complete the recovery of the adsorbed hydrocarbon from the adsorbent. The spent desoxycholic acid having adsorbed thereon the wash hydrocarbon may generally be readily regenerated by heating, steaming or by other methods for restoring the adsorptiveness of the desoxycholic acid for the relatively straight chain aliphatic hydrocarbons of the feed stock in a succeeding run.

The ratio of desoxycholic acid adsorbent to hydrocarbon feed stock mixture supplied to the separation zone is preferably sufficient to provide at least 0.1 mol of desoxycholic acid per mol of the hydrocarbon component in the feed stock mixture to be separated; that is, a molar ratio of desoxycholic acid to the normal or relatively straight chain hydrocarbon component of the feed stock of at least 0.1 to 1 and preferably from about 0.5 to 1 to about 3 to 1 mols per mol.

The present adsorptive-type separation process may be effected in a batch-type procedure or on a continuous basis, provided that sufficient separating agent is maintained in the contacting zone to form a complex between the desoxycholic acid and substantially all of the normal or relatively straight chain components of the feed stock mixture supplied to the separation zone, if substantially complete recovery of these hydrocarbons from a given feed stock is desired. Thus, in a typical batch-type separation process the desoxycholic acid and the feed stock mixture are charged into a suitably stirred or otherwise agitated vessel and the resulting phases mixed for a period of from ½ to about 2 hours and thereafter the resulting adduct or complex is recovered from the resulting slurry by centrifuging, filtration or by other means of separation well known to the art. In a typical continuous type of operation the feed stock mixture and desoxycholic acid are continuously charged into an elongated vertical vessel, the separating agent being preferably introduced into one end of the vessel, the raffinate effluent or stream of unadsorbed components of the feed stock mixture (branched chain and/or cyclic hydrocarbons) being withdrawn from the same end of the vessel that receives the separating agent, while the complex or adduct is withdrawn from the same end of the vessel that receives the feed stock mixture. The adduct may thereafter be transferred to another vertical, elongated vessel (preferably into the top thereof) while a desorbing agent of the aforementioned type is charged into the opposite end of the vessel in order to effect countercurrent desorption, the liquid effluent being thereafter fractionally distilled or otherwise treated to effect separation of the relatively straight chain hydrocarbon recovered from the feed stock from the desorbing or wash hydrocarbon.

The present invention is further illustrated with respect to several of its embodiments in the following examples which, however, are presented merely for illustrative purposes and not by way of limiting the invention.

#### EXAMPLE I

A mixture of 50.1 parts by weight of n-heptane and 49.9 parts by weight of iso-octane was charged into a stirred autoclave, together with 45% by weight of the combined mixture of desoxycholic acid. The resulting mixture was thereafter stirred at 70° C. for ½ hour, followed by filtering the resulting slurry. The filtrate, consisting of unadsorbed hydrocarbon components of the feed stock, was subjected to infra-red analysis to determine the proportion of normal heptane and iso-octane components therein. The analysis indicated that 65% by weight of the filtrate consisted of iso-octane and 35% by weight consisted of n-heptane.

The filter cake recovered from the above filtering operation was stirred with 20% of its weight of n-pentane at 70° C. for ½ hour to form a slurry which was thereafter filtered and the filtrate recovered and analyzed.

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The filtrate consists exclusively of n-pentane and n-heptane.

#### EXAMPLE II

A separation of n-heptane from iso-octane was effected in the following run on a continuous basis and under countercurrent flow conditions by charging the desoxycholic acid continuously into the top of a vertical column packed with desoxycholic acid, as feed stock mixture is continuously charged into the mid-portion of the column. A solid adduct or complex is continuously withdrawn from the bottom of the column, the rate of charging the feed stock mixture being adjusted to provide a n-heptane to desoxycholic acid molecular ratio of 0.5 to 1 by adjusting the flow rates of the adsorbent and feed stock mixture streams into the column. By the method indicated, utilizing a vertical column 40 inches in height, a countercurrent flow arrangement is established and the hydrocarbon stream withdrawn from the top of the column is substantially enriched with iso-octane. A solid desoxycholic acid-n-heptane complex was withdrawn from the bottom of the column as a compressed cake substantially free of liquid phase hydrocarbons. Displacement of the adsorbed hydrocarbon from the complex removed from the bottom of the column with n-pentane, was effected by utilizing sufficient n-pentane to form a thin slurry with the complex at 70° C. and thereafter filtering the resulting n-pentane complex from the resulting mixture of excess n-pentane and the displaced n-heptane. The n-heptane is recovered from the mixture by distillation and on the basis of infra-red analysis of the still residue the n-heptane component is enriched to a product containing about 92% by weight of n-heptane by the indicated countercurrent contacting method. The iso-octane overhead from the above continuous countercurrent column is enriched with iso-octane to a product containing about 95% iso-octane.

#### EXAMPLE III

In the following run a chromatographic adsorption type separation procedure was utilized to determine the effectiveness of solid, crystalline particles of desoxycholic acid as a separating agent in a countercurrent adsorption type of separation procedure. A glass tube 10 inches long by 7 mm. I.D. was packed to a length of 8½ inches with 3.5 grams of crystalline, desoxycholic acid. A hydrocarbon mixture consisting of 50 parts by weight each of iso-octane and n-heptane was charged into the top of the column dropwise, followed by collecting fractions, each representing 10% by volume of the hydrocarbon mixture charged, from the bottom of the column. The test was run at approximately room temperature; that is, about 24° C. and the effluent fractions collected from the bottom were analyzed by infra-red spectroscopy to determine the ratio of iso-octane to n-heptane and thus indicate the effectiveness of the desoxycholic acid for separating the hydrocarbon mixture. The first 10% by weight of the charge stock collected in the effluent receiver contained 60 parts by weight of iso-octane and 40 parts by weight of n-heptane, compared to the 50-50 weight percent mixture charged into the top of the column. The next effluent fraction, comprising from 10 to 20% by weight of the hydrocarbon feed stock contained 55 weight percent iso-octane and 45 weight percent n-heptane.

In a second run utilizing the same feed stock mixture, a similarly packed adsorption column and utilizing the same temperature and collecting procedure, except that cholic acid was substituted for the desoxycholic acid as the packing material in the adsorption column, no discernible enrichment of iso-octane in the effluent fraction was observed, the first 10 ccs. of effluent containing 50 weight percent each of iso-octane and n-heptane (corresponding to the composition of the charging stock). The next 10% by weight of the charge was also of the same

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composition as the feed stock. Thus, cholic acid is ineffective for separating relatively straight chain hydrocarbons from their branched chain homologs.

#### EXAMPLE IV

In the following run, various hydrocarbon mixtures, prepared from C.P. grade materials to form mixtures containing known concentrations of the individual components were utilized in a chromatographic type adsorption procedure to determine the applicability of the method to various hydrocarbon mixtures. The adsorption column consisted of a glass tube 10 inches long by 7 mm. I.D. and the hydrocarbon mixtures were made up by mixing equal weight proportions of a branched chain aliphatic or cyclic hydrocarbon with a relatively straight chain aliphatic hydrocarbon, the mixtures utilized being tabulated in the following Table I which also indicates the degree of separation obtained, as measured by infra-red spectroscopic analyses of the effluent fractions:

Table I

CHROMATOGRAPHIC ADSORPTION OF HYDROCARBONS FROM 50-50 WEIGHT PERCENT MIXTURES

| Mixed Hydrocarbon Charge                                                                 | First Fraction (First 10% by wt. of hydrocarbons charged) | Second Fraction (Second 10% by wt. of hydrocarbon charged) |
|------------------------------------------------------------------------------------------|-----------------------------------------------------------|------------------------------------------------------------|
| n-pentane.....                                                                           | 38.4                                                      | 46.5                                                       |
| isopentane.....                                                                          | 61.8                                                      | 52.4                                                       |
| n-hexane.....                                                                            | 41.3                                                      | 45.1                                                       |
| 2-methylpentane.....                                                                     | 56.1                                                      | 53.2                                                       |
| n-hexane.....                                                                            | 38.2                                                      | 41.2                                                       |
| 2,2-dimethylbutane.....                                                                  | 60.8                                                      | 59.3                                                       |
| n-hexane.....                                                                            | 35.1                                                      | 38.9                                                       |
| cyclohexane.....                                                                         | 63.5                                                      | 58.1                                                       |
| n-dodecane.....                                                                          | 32.1                                                      | 39.2                                                       |
| hydrogenated propylene tetramer comprising various highly branched dodecane isomers..... | 65.4                                                      | 56.3                                                       |

The results indicated above establish the effectiveness of desoxycholic acid for separating hydrocarbon mixtures comprising components of various degrees of branched chain structure, the greatest resolution being obtained between straight chain or normal aliphatic hydrocarbons and their highly branched chain or cyclic isomers.

I claim as my invention:

1. A process for separating a straight chain aliphatic hydrocarbon of from 4 to about 20 carbon atoms per molecule from a mixture thereof with at least one other hydrocarbon component selected from the group consisting of branched chain aliphatic hydrocarbons and cyclic hydrocarbons, which comprises contacting said mixture with desoxycholic acid maintained in solid phase at a temperature of from about 0° to about 120° C. to selectively retain the straight chain hydrocarbon in said acid while rejecting said other hydrocarbon component in a raffinate phase, and separating the raffinate phase from the combination of the desoxycholic acid with the straight chain hydrocarbon.

2. A process for separating a straight chain aliphatic hydrocarbon of from 4 to about 20 carbon atoms per molecule from a mixture thereof with at least one other hydrocarbon component selected from the group consisting of branched chain aliphatic hydrocarbons and cyclic hydrocarbons, which comprises commingling said mixture in liquid phase with solid desoxycholic acid at a temperature of from about 0° to about 120° C. to selectively retain the straight chain hydrocarbon in said acid while rejecting said other hydrocarbon component in a liquid phase, and thereafter filtering the admixed hydrocarbons and desoxycholic acid to separate a filtrate enriched in said other hydrocarbon component from a filter cake comprising a combination of the desoxycholic acid with the straight chain hydrocarbon.

3. The process of claim 1 further characterized in that said straight chain aliphatic hydrocarbon is recovered from

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its combination with the desoxycholic acid by contacting said combination with a desorbing agent comprising a straight chain hydrocarbon having a boiling point which differs from the boiling point of the straight chain aliphatic hydrocarbon of said mixture.

4. The process of claim 3 further characterized in that said desorbing agent comprises n-pentane.

5. The process of claim 3 further characterized in that said desorbing agent comprises n-hexane.

6. The process of claim 1 further characterized in that said hydrocarbon mixture comprises isomeric hydrocarbons.

7. The process of claim 1 further characterized in that said hydrocarbon mixture comprises straight chain and branched chain paraffins.

8. The process of claim 1 further characterized in that said hydrocarbon mixture comprises a straight chain paraffin and a cycloparaffin.

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9. The process of claim 2 further characterized in that said filter cake is thereafter mixed with a straight chain hydrocarbon desorbing agent having a boiling point which differs from the boiling point of the hydrocarbon mixture in an amount sufficient to substantially completely displace the adsorbed hydrocarbon from said desoxycholic acid combination.

10. The process of claim 9 further characterized in that the mixture formed by mixing said combination with said desorbing agent is filtered, the filtrate thereafter distilled and the straight chain aliphatic hydrocarbon component of the feed stock mixture recovered as a fraction of the distillation.

#### References Cited in the file of this patent

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