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SEPARATION OF POLYNUCLEAR FROM MONONUCLEAR AROMATICS

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This invention relates to a process for the separation of polynuclear aromatic compounds from mononuclear aromatic compounds.

Certain higher boiling hydrocarbon fractions such as those obtained in the distillation or conversion of petroleum hydrocarbons contain large quantities of aromatic compounds. For example, many kerosenes have been found to contain 10–30% of aromatic hydrocarbons. These aromatic hydrocarbons comprise both mononuclear aromatics such as alkyl benzenes and polynuclear aromatics such as naphthalene and alkylated derivatives thereof. In addition many higher boiling straight run hydrocarbon fractions contain large quantities of naphthenes which upon thermal or catalytic dehydrogenation are readily converted to aromatics. It will thus be seen that petroleum fractions constitute a potential source of large quantities of both mono- and polynuclear aromatic hydrocarbons. The polynuclear aromatic hydrocarbons are of considerable commercial value, e. g., in the dye industry, but they are not readily convertible into gasoline boiling range hydrocarbons suitable for use in motor fuel. Therefore, by the process of the present invention, a material of relatively little value in the motor fuel industry is separated from other hydrocarbons and is made available as a raw material in other chemical industries.

One object of the present invention is to provide a process for the separation of polynuclear aromatics from mixtures containing polynuclear and mononuclear aromatics by means of a solid adsorbent. Another object of the invention is to provide a convenient method for the separation of alkyl substituted benzenes from polynuclear aromatic hydrocarbons without the necessity of employing special solvent extraction schemes.

In one specific embodiment this invention comprises a process for separating polynuclear from mononuclear aromatics by contacting a hydrocarbon mixture containing alkyl substituted benzenes and polynuclear aromatic hydrocarbons of the fused ring type with a solid adsorbent under such conditions that said polynuclear aromatic hydrocarbons are selectively adsorbed and subsequently recovering said adsorbed polynuclear aromatics.

The charging stocks which may be utilized in the hydrocarbon separation process of this invention may be derived from thermal or catalytically cracked materials, catalytically dehydrogenated or aromatized fractions, etc., or may even be of straight run origin. Charging stocks of exceptionally high total aromatic content may be diluted, preferably with a lower boiling non-aromatic solvent, before processing. Although the invention is directed to the separation of alkyl substituted benzenes (such as triethylbenzene, dibutylbenzene, etc.) from polynuclear aromatic hydrocarbons generally, its preferred application is in the separation of alkyl substituted benzenes from polynuclear aromatic hydrocarbons of the fused ring type, e. g., naphthalene or alkyl substituted naphthalenes, as distinguished from polynuclear aromatics of the bicyclic or non-fused ring type, e. g., biphenyl, terphenyl, polyphenylalkanes, etc.

The method of operation of the invention consists broadly in contacting the mixture of polynuclear and mononuclear aromatics with a solid adsorbent in any convenient manner and under conditions which promote the selective adsorption of the polynuclear compounds. Silica gel is the preferred adsorbent material. However, various other adsorbents may be used, e. g., activated alumina, bauxite, permutites, adsorbent clays and earths, and various appropriate forms of activated charcoal or chars. It should be understood that the various adsorbents are not necessarily equivalent in their effectiveness.

The mechanical details of the method of practicing the invention will depend to a large extent upon the particular adsorbent being used and also upon the nature of the hydrocarbons being separated. In general, I prefer to employ a fixed bed of the solid adsorbent under temperature and pressure conditions such that the hydrocarbons are substantially in the liquid phase during the separation step. This method of operation is particularly desirable when the preferred adsorbent, silica gel, is employed. However, it is not intended to limit the invention to fixed bed operation or liquid phase conditions or to any particular method of contacting the solid adsorbent with the hydrocarbon charging stock. Any suitable processing method may be employed.

When the silica gel adsorbent is used, the process can generally be carried out at substantially atmospheric pressure or slightly superatmospheric pressure and at room temperature or higher. By properly correlating temperature, space velocity, length of processing period, and concentration of diluent (if one is necessary) it is possible to "fractionate" the hydrocarbon mixture by selective adsorption of the polynuclear aromatics on the solid adsorbent. Although the separation can often be effected to a considerable

degree in a single stage treatment, a multistage system may be employed whenever more complete separation is desired.

After an appropriate processing period which must be determined experimentally for each particular adsorbent and charging stock, it is usually necessary to subject the solid adsorbent to a "regeneration" step for the removal of adsorbed polynuclear aromatics. Any convenient method of "regeneration" may be employed among which the following may be mentioned:

(1) Heating the adsorbent solid (under reduced pressure if desired) to vaporize the adsorbed hydrocarbons, and condensing the latter.

(2) Treating the adsorbent with a gas or vapor, e. g., steam or a lower boiling hydrocarbon, at a sufficiently high temperature to effect displacement or desorption of the polynuclear aromatics.

(3) Treating the adsorbent with a liquid, e. g., water or a liquid hydrocarbon, at a sufficiently high temperature to effect displacement or desorption of the polynuclear aromatics.

The effluent hydrocarbon stream from the adsorption zone contains relatively large quantities of mononuclear aromatics and if desired these can be separated from non-aromatic contaminants which may be present. The latter separation is readily carried out by any suitable method well-known to the art for the separation of mononuclear aromatics from non-aromatic hydrocarbons. Among the methods which may be employed are: (1) an adsorption system similar to that used for the separation of mononuclear from polynuclear aromatics, (2) various solvent extraction schemes, and (3) distillation in cases wherein the non-aromatic contaminant has a different boiling range from that of the mononuclear aromatics.

In general, when the adsorbent solid has been utilized for a sufficient length of time so that its effectiveness in the selective adsorption of the polynuclear aromatics begins to decline, it will be necessary to "regenerate" the adsorbent by any of the hereinbefore described methods for removing the adsorbed materials. However, in certain types of "regeneration" procedures it is also necessary to remove the regenerating medium from the adsorbent before processing is resumed. This is particularly true if water has been employed to displace the adsorbed polynuclear aromatics. The water may conveniently be removed from the adsorbent by a drying procedure, e. g., by passing a stream of warm air or gas through the adsorbent zone. In some cases using adsorbents such as silica gel, periodic treatment of the adsorbent by oxidation may be necessary in order to effect complete restoration of the efficiency of the adsorbent for the mononuclear-polynuclear aromatic separation.

The following examples illustrate one specific operation of the process. It is not intended, however, to limit the invention in any way to the details described therein. These examples are merely an illustration of the nature of the separations which may be accomplished by the use of the process described.

Example I

A charging stock was prepared which consisted of 46% by weight of triethylbenzene having a refractive index of 1.4997 and 54% by weight of alphamethylnaphthalene having a refractive index of 1.6070. A fixed bed of 75 cc. of 12–20 mesh silica gel was employed as an adsorption zone. The total depth of the bed was approximately 14 inches.

The charging stock was diluted to five times its original volume with pentane and 82 cc. of this solution was passed downwardly through the 14 inch bed of a silica gel at room temperature for a period of 2.7 hours. The pertinent experimental data from the test are shown in Table I below:

Table I

Cut No.	Grams of aromatics	Weight percent on aromatics charge	n_D^{20}	Composition, weight percent	
				Triethylbenzene	α-Methylnaphthalene
1	0.21	1.4	1.4809		
2	2.55	16.4	1.5143	84	16
3	3.59	23.2	1.5410	57.5	42.5
4	7.18	46.4	1.5787	23	77
Total	13.53	87.4			

Cuts 1 and 2 comprised the first two 25 cc. portions of recovered liquid. Cut 3 consisted of the next 29 cc. of recovered liquid obtained by flushing the adsorbent with a 25 cc. portion of fresh pentane. Cut 4 consisted of the recovered adsorbed hydrocarbons displaced from the silica gel by flushing with 50 cc. of water and an additional 25 cc. of pentane. Aromatics were recovered from each cut by distilling off the pentane, and the percentage of each of the aromatic constituents was determined from refractive indices.

It will be noted that the refractive index of Cut 1 is lower than that of either of the two starting materials. This is caused by the presence of traces of impurities in one or both of the constituents of the charging stock.

Example II

All of Cut 4 from the above experiment was diluted with 30 cc. of pentane and the solution was passed downwardly at room temperature through a 16 inch bed of 37 cc. fresh silica gel over a period of one hour. The pertinent data from this experiment are shown below in Table II.

Table II

Cut No.	Grams of aromatics	Weight percent on aromatics charge	n_D^{20}	Composition, weight percent	
				Triethylbenzene	α-Methylnaphthalene
1	3.46	48.5	1.5669	34	66
2	1.80	25.2	1.5963	8.6	91.4
Total	5.26	73.7			

Cut 1 consisted of 20.5 cc. of liquid which drained from the bed plus an additional 35.5 cc. obtained by flushing with 37 cc. of fresh pentane. Cut 2 comprised the recovered adsorbed hydrocarbons displaced from the adsorbent by flushing with 50 cc. of water followed by 25 cc. of pentane. The methods of recovery and analysis of the aromatics were the same as those described in connection with Example I.

These experiments show that a substantial separation of the mononuclear aromatic from the polynuclear aromatic was effected by passing a mixture of the two constituents through silica gel. The unadsorbed triethylbenzene was concentrated in the first cuts and the polynuclear

alpha-methylnaphthalene was concentrated in the last cuts. The benefits of multi-pass treatment are evident from the increased concentration of the polynuclear aromatic shown in Example II.

I claim as my invention:

1. A process for separating mononuclear from polynuclear aromatic compounds which comprises contacting a mixture of said aromatic compounds in liquid phase with a solid adsorbent whereby to selectively adsorb the polynuclear aromatic compounds on said solid adsorbent and subsequently recovering said polynuclear aromatic compounds from said adsorbent.

2. A process for the separation of aromatic hydrocarbons which comprises contacting a mixture containing mononuclear and polynuclear aromatic hydrocarbons in liquid phase with a solid adsorbent under conditions such that the polynuclear aromatic hydrocarbons are selectively adsorbed, subsequently recovering polynuclear aromatic hydrocarbons from said adsorbent, and separating mononuclear aromatic hydrocarbons from the unadsorbed hydrocarbons.

3. The process of claim 1 wherein said solid adsorbent comprises silica gel.

4. A process for the separation of alkyl substituted benzenes from polynuclear aromatic hydrocarbons which comprises contacting a mixture containing said hydrocarbons in liquid phase with a solid adsorbent whereby to selectively adsorb said polynuclear aromatic hydrocarbons.

5. A process for the separation of alkyl substituted benzenes from polynuclear aromatic hydrocarbons of the fused ring type which comprises contacting a mixture containing said hydrocarbons in liquid phase with a solid adsorbent under conditions suitable for the selective adsorption of said polynuclear aromatic hydrocarbons.

6. The process of claim 5 wherein said solid adsorbent comprises silica gel.

7. The process of claim 5 wherein said adsorbed hydrocarbons are recovered by introducing into the absorption zone a non-aromatic hydrocarbon at a temperature sufficient to desorb the polynuclear aromatic hydrocarbons from the solid adsorbent.

8. The process of claim 5 wherein said adsorbed hydrocarbons are recovered by introducing steam into said adsorption zone whereby to desorb the polynuclear aromatic hydrocarbons from the solid adsorbent.

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