Sept. 5, 1972 L. J. E. HOFER ET AL 3,689,404

SEPARATION OF HYDROCARBONS WITH ACTIVATED CARBON

Filed April 5, 1971 2 Sheets-Sheet 1

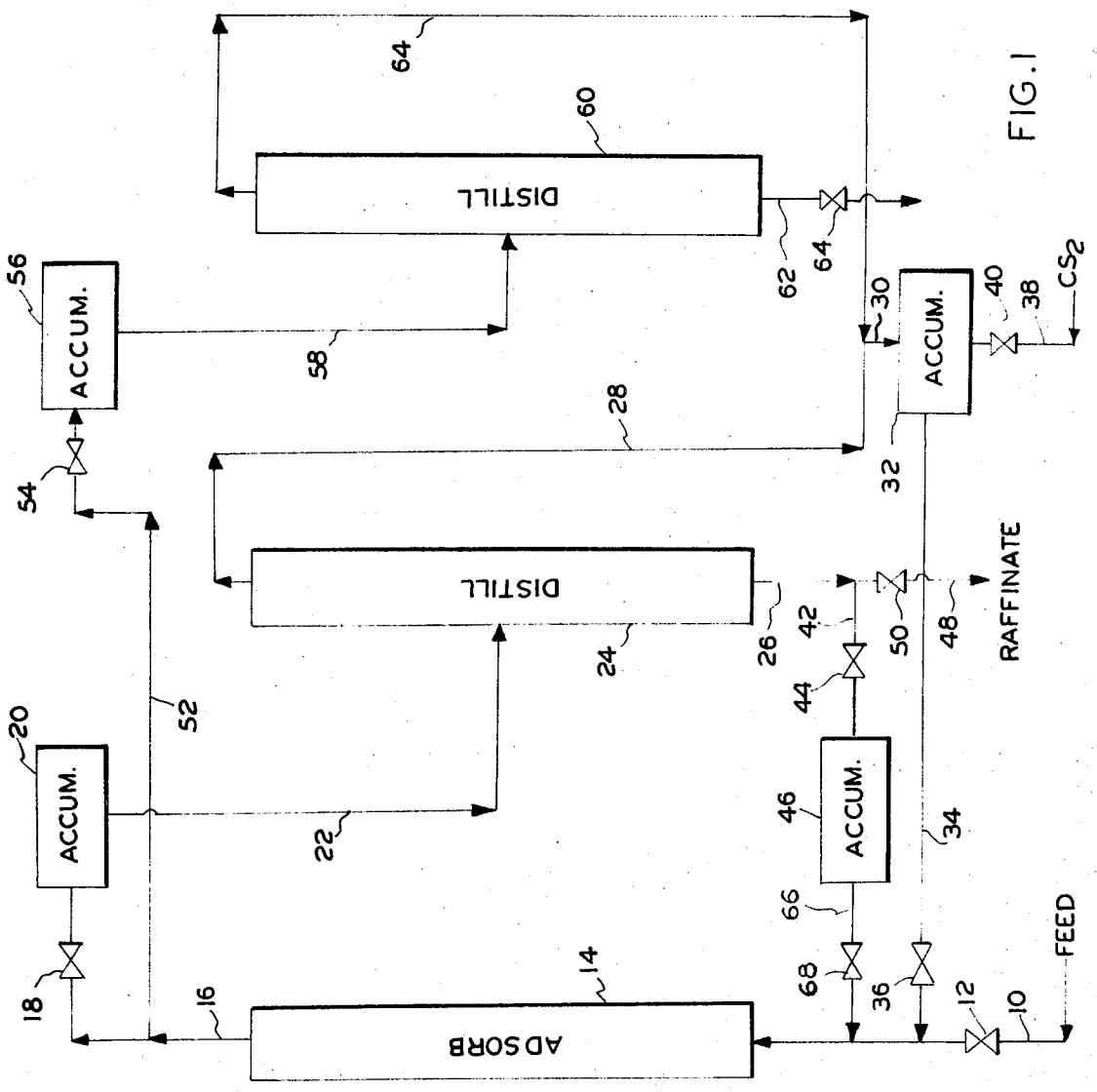


FIG. 1

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SEPARATION OF HYDROCARBONS WITH ACTIVATED CARBON

Filed April 5, 1971 2 Sheets-Sheet 2

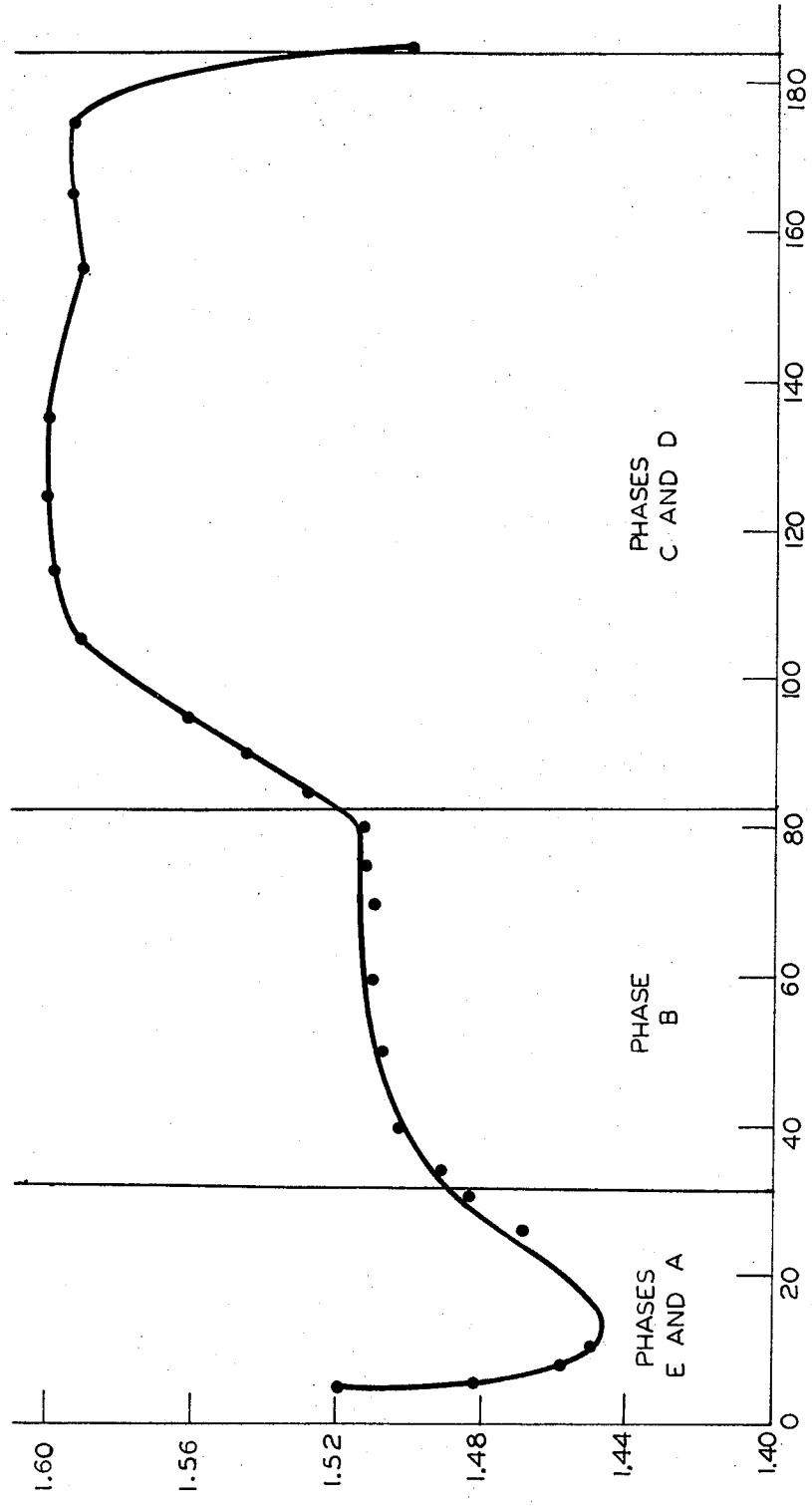


FIG.2

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United States Patent Office 3,689,404 Patented Sept. 5, 1972

3,689,404

SEPARATION OF HYDROCARBONS WITH ACTIVATED CARBON

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Filed Apr. 5, 1971, Ser. No. 131,054
Int. Cl. C07c 7/12
U.S. Cl. 208—310 18 Claims

ABSTRACT OF THE DISCLOSURE

Hydrocarbon mixtures, such as light cycle oils from a catalytic cracking unit, paraffinic lubricating oils and the like, are selectively separated by a cyclic adsorption technique involving passing the hydrocarbon mixture through a fixed bed of activated carbon to adsorb selectively more readily adsorbed components or an adsorbate phase while collecting less readily adsorbed components or a raffinate phase; passing a first portion of a predetermined volume of carbon disulfide through the carbon to displace the adsorbate phase while collecting a portion of the raffinate phase as a recycle stream; passing the remainder of the carbon disulfide through the carbon while collecting an adsorbate phase; passing a first portion of the collected recycle material through the carbon while collecting an adsorbate phase; passing the remainder of the collected recycle material through the carbon while collecting a raffinate phase; and separating carbon disulfide from the raffinate and adsorbate phase for reuse as a displacing fluid.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to the separation of hydrocarbon mixtures. More specifically, the present invention relates to the separation of aromatic hydrocarbons from mixtures of such aromatic hydrocarbons with aliphatic hydrocarbons. Still more specifically, the present invention relates to the separation of polycyclic aromatics from a light cycle oil of a catalytic cracking operation by contacting the cycle oil with activated carbon to selectively adsorb the polycyclic aromatics and thereafter displacing the polycyclic aromatics with carbon disulfide.

Description of the prior art

Many refinery operations require the separation of various types of hydrocarbons from one another. In many cases, aromatic hydrocarbons, such as benzene, toluene, xylenes, naphthalenes and the like, must be recovered or separated from mixtures of the same with aliphatic hydrocarbons or from one another. Such separations are generally carried out for the purpose of producing chemical grade aromatics or for improving the quality of certain low grade hydrocarbon fractions.

One of the primary products sought to be recovered in refinery operations because of its commercial value is naphthalene. The chemical importance of naphthalene resides primarily in its use as an intermediate in the production of phthalic anhydride. For example, roughly 80% of all of the naphthalene produced domestically is consumed in the production of phthalic anhydride.

Heretofore, the primary source of naphthalene has been coal tar fractions. However, the uncertainties and fluctuations in the production of coal tars makes it undesirable to tie the production of naphthalene to such variable sources, particularly since the major portion of coal tar is produced as a by-product of the manufacture of coke for the production of steel.

Naphthalene does not exist in any great volumes in

crude petroleum hydrocarbons. While the amounts of naphthalene in crude oils varies to some extent, the total of all aromatic hydrocarbons in petroleum is usually only about 5%. Accordingly, it is impractical to separate such naphthalene from the crude by simple distillation, since a number of other contaminating materials boil in the same boiling range. However, certain refined petroleum fractions, such as fractions obtained as products of catalytic reforming, catalytic cracking and thermal cracking, do contain significant quantities of naphthalene and alkyl-substituted naphthalenes to be of interest as feedstocks for further processing. Some feedstocks, and, particularly, products of catalytic cracking contain large quantities of naphthalene and alkyl-substituted naphthalenes and only minor quantities of monocyclic aromatic and paraffins. These feeds may, therefore, be directly processed to convert the alkyl naphthalenes to naphthalene. However, when attempting to process fractions containing smaller amounts of naphthalene precursors, it becomes impractical and prohibitively expensive, to convert this feed to naphthalene.

While a number of techniques for concentrating naphthalene precursors have been tested in the past, and found useful to a greater or lesser extent, few have been found to economically produce substantial quantities of naphthalene precursors which, in turn, produce economic yields of naphthalene. However, one effective technique has been the utilization of solvents for the separation of paraffins and monocyclic hydrocarbons from dicyclic or polycyclic hydrocarbons in the feed material. While such solvents are effective in varying degrees, the commercial use of such solvents has been practically nil. There are believed to be several basic reasons for such lack of utility and these are primarily directed to the amount of solvent required and hence the cost of operation. In addition, there is a limit to the degree of separation which can be practically and economically effected by the use of a solvent. Even after concentration of polycyclic hydrocarbons by the use of a solvent, there still remain paraffinic and monocyclic aromatic hydrocarbons which boil in substantially the same range as the polycyclic hydrocarbons of interest.

Another problem area in the processing of petroleum products is the treatment of wax distillates. Wax distillates are lubricating oil distillates from petroleum. Normally, these materials are dewaxed, earth treated and filtered to produce neutral lubricating oils and wax. However, due to the presence therein of aromatics, the products have a very poor viscosity index and a dark color, thereby making them undesirable for their intended purpose. At present, there is no satisfactory technique for removing the aromatics.

It is also known that numerous other petroleum or coal liquid streams could be greatly improved if there were some simple and economic manner of separating hydrocarbons by type and particularly separating aromatics from non-aromatics.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide an improved method for the separation of hydrocarbons. Another and further object of the present invention is to provide an improved method for the separation of aromatic hydrocarbons from aliphatic hydrocarbons. Yet another object of the present invention is to provide an improved method for the separation of high concentrations of polycyclic hydrocarbons from hydrocarbon mixtures containing the same. Another object of the present invention is to provide an improved method for the production of polycyclic hydrocarbons from petroleum hydrocarbon mixtures. A still further object of the present invention is to provide an improved method for the

production of polycyclic hydrocarbons from catalytic light cycle oils obtained from the catalytic cracking of petroleum hydrocarbons. Another and further object of the present invention is to provide an improved method for the production of polycyclic hydrocarbons by passing a petroleum hydrocarbon mixture containing paraffins, monocyclic aromatics, and dicyclic aromatics, through an adsorbent to separate dicyclic aromatics therefrom. A still further object of the present invention is to provide an improved method for the production of polycyclic hydrocarbons wherein a catalytic light cyclic oil is subjected to adsorption with an activated carbon, a raffinate phase is collected, adsorbate is displaced with carbon disulfide, the adsorbate phase is separated from the displacing fluid, and the displacing fluid is recycled to the adsorption step. Another object of the present invention is to provide an improved method for the separation of dicyclic hydrocarbons from mixtures of dicyclic, monocyclic and paraffinic hydrocarbons. Another and further object of the present invention is to provide an improved method for the recovery of polycyclic aromatics from mixtures of polycyclic aromatics, monocyclic aromatics and paraffins wherein the mixture is subjected to contact with an activated carbon and the activated carbon is displaced with carbon disulfide. Yet another object of the present invention is to provide an improved process for improving the viscosity index of lubricating oils. Another and further object of the present invention is to provide an improved process for removing aromatic hydrocarbons from lubricating oils.

These and other objects and advantages of the present invention will be apparent from the following detailed description.

BRIEF DESCRIPTION OF THE INVENTION

Briefly, in accordance with the present invention, hydrocarbon mixtures are separated into constituent groups, particularly into aromatic versus aliphatic hydrocarbons, polycyclic aromatics versus monocyclic aromatics and the like, by passing the mixture through activated carbon to produce an effluent raffinate phase of the least readily adsorbed material and selectively adsorbing a more readily adsorbed material; passing carbon disulfide through the activated carbon containing the selectively adsorbed adsorbate to displace the same, and recovering the displaced adsorbate. Where the hydrocarbon mixture contains substantial volumes of polycyclic aromatics, the process is utilized to selectively adsorb such polycyclic aromatics.

The present invention will be more clearly understood by reference to the drawings when read in conjunction with the following detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

The details of the present invention will be better understood by reference to the drawings, wherein:

FIG. 1 is a flow diagram illustrating the overall method of the present invention; and

FIG. 2 is a plot of refractive index versus time for a single cycle of operation in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

As will be illustrated by the following description, it has been found that the refractive index of the effluent from the adsorbtion column of the present invention or a time cycle may be effectively utilized to control the operation of the process of the present invention.

In accordance with FIG. 1 of the drawings, a liquid hydrocarbon feed material is introduced through line **10** and valve **12** to fixed bed adsorption column **14** and thence upwardly through the column. Adsorption column **14** is, of course, filled with a granular activated carbon which will selectively adsorb certain of the components of the feed material. The effluent from column **14**, comprising the non-adsorbed components (raffinate phase), is discharged through line **16** and valve **18** to accumulator **20**. Thereafter, the feed to column **14** is switched from hydrocarbon feed material to carbon disulfide and a predetermined volume of carbon disulfide is passed through column **14**. During the initial startup of the system, both the point of termination of hydrocarbon feed and the predetermined volume of carbon disulfide can be determined experimentally by observing a characteristic of the raffinate phase and/or the adsorbate phase (preferentially adsorbed components), and adjusting the point of termination of the hydrocarbon feed and the volume of carbon disulfide until raffinate and/or adsorbate of the desired character is obtained. For example, the refractive indices of the raffinate and adsorbate phases may be observed, as will be more fully explained hereinafter. Once the point of termination of hydrocarbon feed and the volume of carbon disulfide have been established the system will have reached steady state conditions and the entire operation can be repeated on the cyclic operating basis hereinafter explained in detail. Sometime after introduction of carbon disulfide is begun, the raffinate effluent will contain carbon disulfide. In order to separate the raffinate from the carbon disulfide, the effluent from accumulator **20** is passed through line **22** to distillation column **24**. In distillation column **24** this mixture of raffinate and carbon disulfide is separated and the raffinate is discharged through line **26** while the carbon disulfide is discharged through line **26**, and, thence, through line **30** to accumulator **32**. Carbon disulfide is fed from accumulator **32** through line **34** and valve **36** to the adsorption column **14**. Where necessary, makeup carbon disulfide is introduced to accumulator **32** through line **38** and valve **40**. The introduction of carbon disulfide to column **14** is carried out in two distinct phases. During the introduction of a first portion of carbon disulfide, raffinate discharged through line **26** of distillation column **24** is passed through line **42** and valve **44** to recycle accumulator **46**. The amount of raffinate collected at this point can also be determined by any convenient means. The portions of raffinate which are not collected in accumulator **46** may constitute the more desirable components of the feed material or the less desirable components of the feed material depending, of course, upon the nature of the feed material. For example, where a light cycle oil is to be separated, primarily for the recovery of dicycle hydrocarbons, the raffinate phase will be the less desirable monocyclic and paraffinic materials. On the other hand, where a paraffinic lubricating oil is treated to improve its viscosity index, the raffinate is the primary product. In any event, raffinate which is not collected may be withdrawn from distillation column **24** through line **48** and valve **50**. The raffinate may be stored or otherwise utilized. After the first portion of carbon disulfide has been utilized, the second portion of a predetermined amount of carbon disulfide is passed through adsorption column **14**. While the second portion of carbon disulfide is being passed through column **14**, an adsorbed or adsorbate phase is passed through line **52** and valve **54** to adsorbate accumulator **56**. This adsorbate stream comprises a mixture of the preferentially adsorbed components of the feed mixture and carbon disulfide. The adsorbate passes from accumulator **56** through line **58** to distillation column **60**. In distillation column **60**, the adsorbate is stripped of carbon disulfide and discharged through line **62** and valve **64** while the carbon disulfide is passed through line **64**, and, thence, through line **30** to accumulator **32**. After the predetermined volume of carbon disulfide has been utilized, the recycle raffinate collected in accumulator **46** is passed through line **66** and valve **68** as a recycle to adsorption column **14**. The introduction of recycle to adsorption column **14** is also carried out in two separate phases. As a first portion of the recycle material is passed through adsorption column **14**, the effluent from column **14** constitutes a further portion of the adsorbate phase which is collected and distilled as previously indicated. The end of the first recycle phase is determined in accordance with the previously mentioned

criteria for controlling the operation. Thereafter, the second portion of recycle is passed through column **14** until all of the collected recycle has been used. During the introduction of this second portion of the recycle, the effluent from the adsorption column is switched to the raffinate handling portion of the system and thus is accumulated in accumulator **20** and distilled in distillation column **24**. The raffinate is then treated as previously described.

A suitable activated carbon for use in accordance with this present invention may have a broad range of particle sizes, for example 4 x 6 to 20 x 50 mesh size (U.S. sieve series). The following physical properties are also desirable:

Total Surface Area (N_2, BET Method [1]), $m.^2/g.$	500–1500
Apparent density (bulk density, dense packing), g./cc.	0.3–0.6
lb./ft.^{3}	20–30
Particle Density (Hg displacement), g./cc.	0.5–1.0
Real density (He displacement), g./cc.	2.0–2.2
Pore volume (within particle), cc./g.	0.5–1.5
Voids in dense packed column, percent	20–50
Specific heat at 100° C.	0.2–0.3

[1] Brunauer, Emmett and Teller: J. Am. Chem. Soc. 60, 309 (1938).

The following examples illustrate the practice of the present invention and compare the same with similar techniques.

In all of the examples, the activated carbon utilized as an adsorbent is formed from bituminous coal combined with suitable binders and is activated with steam at a high temperature. The particle size is 12 x 40 mesh size (U.S. sieve series). This activated carbon had the following physical properties.

TABLE I

Physical properties activated carbon

Total surface area (N_2, BET Method [1]), $m.^2/g.$	1000–1100
Apparent Density (bulk density, dense packing), g./cc.	0.44
lb./ft.^{3}	27.5
Particle density (Hg displacement), g./cc.	0.78
Real density (He displacement), g./cc.	2.1
Pore volume (within particle), cc./g.	0.81
Voids in dense packed column, percent	44
Specific heat at 100° C.	0.25

[1] Brunauer, Emmett and Teller: J. Am. Chem. Soc. 60, 309 (1938).

Except where otherwise noted, the feed material employed was a 430 to 550° F. cut of a light cycle oil from the catalytic cracking operation. Table II below lists the properties of a typical feed material of this type.

TABLE II

Properties of Light Cycle Oil

ASTM distillation, ° F.:	
IBP	434
5	450
10	454
20	464
30	470
40	474
50	480
60	484
70	491
80	497
90	508
95	518
EP	530
API gravity at 60°	26.5
Specific gravity 60/60	0.896
n_D^{20}	1.5145
COC° F.:	
Flash	220
Fire	225
FIA:	
PN	33.2
O	4.3
A	62.5

Table III below summarizes four cycles of adsorption-displacement wherein a light cycle oil heart cut was adsorbed on activated carbon and thereafter displaced by steam stripping at 600° F. It is to be observed that steam stripping is relatively ineffective. The capacity of the carbon decreases very sharply throughout the adsorption-displacement when utilizing steam as a recovery agent. In addition, when polycyclic aromatics are to be separated, the refractive index of the effluent raffinate should be below about 1.5. In the run illustrated, the raffinate refractive index was below that figure for only about 5 to 10 minutes and it rapidly increased to that of the feed material (about 1.5163) after only 18 to 20 minutes. The refractive index of the adsorbate is also too low since polycyclic concentrates should have a refractive index above about 1.54 and preferably near 1.6. Where the refractive index of a stream, such as raffinate or adsorbate, is referred to, this represents the refractive index of the particular steam after carbon disulfide has been removed therefrom.

TABLE III

Steam Stripping of Carbon

Cycle	1	2	4	5
Charge				
Refractive index	1.5163	1.5163		
Weight, gms.	2,504	2,340	1,968	2,220
Pumped effluent	1,130	1,248	851	1,154
Blowdown, gms.	696	526	797	780
Grams adsorbed (by diff.)	678	566	320	286
Recovery, gms.	548		261	227
Loss, gms.	130		59	59
Adsorbate RI	1.5318			

A second test was made with the same feed material, the same activated carbon, and in the same equipment but with carbon disulfide as the displacing agent. The results of this test are set forth in Table IV below. It is obvious from Table IV that the capacity of the carbon bed decreased over the first several cycles, but then remained substantially constant. Also, except for the first run when the carbon was dry, the time needed to reach an effluent refractive index of 1.5 after collection of the first effluent, was about 10 to 20 minutes. This is more than twice the length of time observed when steam stripping. This shows that the use of carbon disulfide as a displacing media not only provides high carbon capacity but it also gives a higher selectivity for the polycyclic hydrocarbons sought to be extracted from the light cycle oil. Thus, carbon disulfide displacement results in a higher overall carbon capacity and a higher yield of the polycyclic hydrocarbon materials. This higher yield of the polycyclic hydrocarbon materials is a function of the higher equilibrium capacity of the carbon, the ability of the carbon disulfide to effectively displace these polycyclic hydrocarbon materials, and the higher selectivity for polycyclic hydrocarbon materials which the carbon disulfide imparts to the carbon.

TABLE IV

Carbon Disulfide Displacement

Cycle	1	2	3	4	5	6
Charged						
Refractive Index	1.5160	1.5160	1.5160	1.5160	1.5160	1.5160
Weight, gms.	2,252	2,687	2,651	2,661	2,678	2,685
Pumped effluent, gms.	896	1,213	1,246	1,286	1,690	1,281
Blowdown, gms.	652	706	725	706	304	729
Total raffinate, gms.	1,548	1,919	1,971	1,992	1,994	2,010
"Adsorbate," gms.	704	768	680	669	684	675
Recovery, gms.	641	700	724	664	669	643
Gain or loss, gms.	−63	−68	+44	+5	−15	−32
Vol. pumped in at 1st effluent, cc.	1,435	960	990	870	820	825
Time to 1st effluent, min.	62	37	40	39	38	35

The quality of adsorbate from the two previous tests is given below.

Gas chromatograph	Feed	Adsorbate quality (Table III runs) steam stripped adsorbate	(Table IV runs) CS_2 stripped adsorbate Cycle 1	Cycle 2	Cycle 3
<βMN	51.0	47.0	40.9	41.7	41.7
βMN	9.6	9.4	8.2	7.4	7.2
αMN		4.7	4.5	4.2	4.1
DMN + biphenyl	19.3	23.9	26.9	26.8	27.9
Ace. +	20.1	15.0	19.5	19.9	19.1

A series of runs was made also in order to determine whether benzene could be utilized as a displacing medium. While benzene was found to be a fairly effective displacing medium, such displacement required volumetric ratios of benzene to light cycle oil feed of 10 to 1 or greater, in order to recover 95% or more of the light cycle oil hydrocarbons from the adsorbent. This becomes economically prohibitive.

Table V below summarizes an adsorption-displacement run in which recycle of a selected portion of the effluent material was practiced. It is to be noted from Table V that collection of recycle material was terminated during the cycle when the refractive index of the effluent being collected for recycle material reached 1.52. As is pointed out hereinafter, this is an optimum cut point for the recycle operation when utilizing refractive index as a control and selectively adsorbing polycyclic hydrocarbons.

TABLE V

Fresh feed, gms.	579
Fresh feed, ccs.	640
Recycle feed, gms.	772
Recycle feed, ccs.	860
Raffinate:	
Weight, gms.	199
Final RI	1.489
Average RI	1.476
Naphthalene precursors, percent	5.2
Yield, wt. percent	36.3
Recycle:	
Weight, gms.	807
Volume, ccs.	900
Initial RI	1.489
Final RI	1.520
Average RI	1.512
Adsorbate:	
Weight, gms.	349
Average RI	1.550
Naphthalene precursors, percent	51.3
Yield, wt. percent	63.7
Naphthalene precursors recovered, percent on feed	32.7
Cycle time, minutes	255
Adsorption rate, ccs./min.	11.5
Desorption rate, ccs./min.	23.0
Vol. CS_2, ccs.	3000
No blowdown after adsorption	
Blowdown after desorption	

As a result of the conduct of operations utilizing a recycle phase and the conduct of tests while varying other conditions of operation, it was ultimately determined that the process of the present invention could most effectively be carried out by a cycle of operation involving adsorption and displacement in which five distinct phases were practiced. Table VI below illustrates the general character of this five-phase operation.

TABLE VI

Phase	In	Out	Valves open	Termination of phase
A	Feed	Raffinate + CS_2	12, 18 and 50.	When RI of raffinate reaches 1.49.
B	CS_2	Recycle	36, 18 and 44.	When RI of recycle reaches 1.58.
C	CS_2	Adsorbate + CS_2	36, 54 and 68 or 76.	When all of predetermined volume of CS_2 is used.
D	Recycle	do	72, 54 and 68 or 76.	When RI of adsorbate reaches 1.52.
E	do	Raffinate + CS_2	72, 18 and 50.	When all of collected recycle is used.

In the operation of the adsorption-displacement cycle, as illustrated in the Table VI above, the operation is broken down into five phases. It has been found in accordance with the present invention that switching of the input and output of adsorption column **14** from one phase to the next can be conveniently handled by monitoring the output stream and performing the switching operation at such times as certain refractive indices are measured. It has been found in accordance with the present invention that the refractive index of the effluent is an excellent measure of how the adsorption column is operating and when each phase of the operation is essentially completed. The refractive index is, of course, an excellent indicator of the character of hydrocarbons since pure alkyl naphthalenes normally have a refractive index of about 1.6, monocyclic hydrocarbons have lower refractive indices and paraffinic hydrocarbons have still lower refractive indices.

Referring now to the above Table VI, it is to be seen that during Phase A of the operation, the light cycle oil feed is introduced to the system by opening valve **12** and the nonadsorbed raffinate is passed through valves **18** and ultimately **50** for collection or further use. This phase of the operation is continued until the refractive index of the raffinate effluent reaches a value of about 1.49. At this time, valve **36** is opened to introduce carbon disulfide to adsorption column **14** and Phase B of the operation is started. During Phase B of the operation, valves **18** and **44** are opened to collect recycle material in accumulator **46**. Phase B of the operation continues until the refractive index of the recycle effluent stream being collected reaches a value of about 1.58. It is to be noted that the refractive index of the recycle is the primary control point. At this point, Phase C of the operation begins. During Phase C of the operation, valve **36** remains open and carbon disulfide continues to be passed through adsorption column **14**. However, valve **54** is opened to discharge adsorbate to adsorbate accumulator **56**—the raffinate valve **18** being closed. After a predetermined volume of carbon disulfide displacing fluid has been utilized, Phase C of the operation is terminated and Phase D is begun by opening valve **72** to begin the passage of recycle fluid from accumulator **46** through adsorption column **14**. At the same time, valve **54** remains open to discharge adsorbate to accumulator **56**. The adsorbate ultimately passes through valves **68** or **76**. When the refractive index of the adsorbate reaches a value of about 1.52, Phase D is terminated and Phase E begins. During Phase E of the operation, recycle is continued through valve **72** until all of the collected recycle effluent is used and valves **18** and **50** are opened to discharge a further portion of raffinate phase. When all of the collected recycle material has been passed through adsorption column **14**, Phase E is terminated and the next cycle is begun by switching to a Phase A operation. The volumes of materials handled during a complete cycle and, of course, the sizing of the equipment utilized in the operation are, of course selected so that sufficient polycyclic aromatics are collected in accumulator **42** to continuously operate the remainder of the hydrogen treating and hydrodealkylating operations.

While specific refractive indices are given by way of example, the process can be varied depending upon the nature of the feed and the desired end product. Effective results can be obtained by selecting refractive indices as follows:

End of Phase A	1.45–1.55
End of Phase B	1.47–1.59
End of Phase D	1.45–1.55

Table VII below summarizes an optimum treatment of light cycle oil feed when carried out in the five-phase cyclic manner set forth in Table VI.

TABLE VII

Fresh feed, gms.	533
Fresh feed, ccs.	595
Recycle feed, gms.	854
Recycle feed, ccs.	950
Raffinate:	
Weight, gms.	217
Final RI	1.495
Average RI	1.475
Recycle:	
Weight, gms.	872
Volume, ccs.	980
Initial RI	1.495
Final RI	1.523
Average RI	1.523
Adsorbate:	
Weight, gms.	304
Average RI	1.552
Naphthalene precursors, percent	56.1
Yield, wt. percent	58.3
Naphthalene precursors recovered, percent on feed	32.7
Cycle time, minutes	150
Adsorption rate, ccs./min.	23.0
Desorption rate, ccs./min.	23.0
CS_2 vol., ccs.	2000
No blowdown after adsorption	
No blowdown after desorption	

The first column of Table VIII compares operation in accordance with the present invention when the activated carbon had been used for six cycles of adsorption-displacement with a similar operation as set forth in column two where the carbon had been used for seventy-nine cycles of adsorption-displacement. It is, of course, quite obvious from the data of Table VIII that no observable deactivation of the carbon takes place and it is just as effective after the 79th cycle as it was after the 6th cycle.

TABLE VIII

Fresh feed, gms.	867	859
Fresh feed, cc.	940	960
Recycle feed, gms.	420	460
Recycle feed, cc.	470	505
Column length, ft.	8	8
Raffinate:		
Weight, gms.	173	186
Final RI	1.492	1.494
Average RI	1.467	1.471
Recycle:		
Weight, gms.	426	256
Average RI	[1] 1.515	[1] 1.515
Adsorbate:		
Weight, gms.	652	662
Average RI	1.533	1.531
Naphthalene Precursors, percent	43.0	45.5
Yield, wt. percent	79.0	78.1
Naphthalene precursors, percent on feed	34.0	35.5
CS_2 used, cc.	3,000	3,000
Cycle time, min.	370	212
Desorption rate, cc./min.	11.5	22
Adsorption rate, cc./min.	11.5	22

[1] Blowdown used.

Finally, Table IX of the examples shows the effectiveness of the process of the present invention on the removal of aromatics from a wax distillate of a low grade Pennsylvania crude oil. It is obvious from the data of Table IX that the adsorption technique is effective in the removal of aromatics from the wax distillate. This is so since aromatics are heavier and more viscous than paraffinic materials, they have a very poor viscosity index and are dark in color. Consequently, the removal of such aromatics from the wax distillate produces an effluent product having a much lower viscosity, an improved viscosity index and a lighter color. On the other hand, the adsorbate or aromatic fraction has an extremely low API gravity, a high viscosity at 100° F., a negative viscosity index and is almost black in color.

TABLE IX

Adsorption of Wax Distillate

	Feed	Effluent	Adsorbate
Gravity, ° API	31.4	34.9	11.9
Viscosity at 100° F., SUS	83.15	79.66	149.8
Viscosity at 210° F., SUS	38.05	37.67	40.03
Viscosity index	111	117	−34
Pour point, ° F.	+75	+60	+50
Color	2−	0.5	7.5

It is also quite obvious that other hydrocarbon materials may be separated in accordance with the present invention, including heavy oils, such as vacuum tower bottoms, etc. The only limitations on the type of material treated appear to be that there be no suspended solids in the liquid and the operating temperature should not be over 100° F., since such high temperatures cause the carbon disulfide to decompose. Hence, any material which is too viscous to pass through the column at temperatures below 100° F. should not be utilized in the process. However, such materials may be diluted with an appropriate solvent to permit handling in this process. Operation should not be conducted below 60° F. and preferably, not below 75° F. Column pressures of 15 to 35 p.s.i. are suitable.

As a general proposition, flow rates of feed, displacing fluid and recycle may vary anywhere between 0.05 gallon per minute per square foot of cross-section of the carbon column to as high as 10 gallons per minute per square foot. A preferred rate is 2.0 to 4.5 gallons per minute per square foot for feed and displacing fluid. Experimentation has shown that there is no real advantage in utilizing a column greater than about 10 feet in length. However, by doubling the length of the bed, the flow rate can be doubled and plant capacity increased accordingly. The recycle feed rate is preferably 3.5 to 5.0. The carbon disulfide-to-feed ratio may also vary considerably. This ratio should be at least 1 to 1 but may be anywhere above this limit. As the previous data has indicated, it is possible to recover a very pure methyl naphthalene fraction by increasing the amount of carbon disulfide employed. However, this increases the expense of removing carbon disulfide from the product. The use of high carbon disulfide ratios also requires increased capital investment due to the fact that the carbon disulfide is toxic and explosive.

Once a cycle of operation has been set up based on the refractive index cut point or some other measure of product quality, time-cycle control can be utilized to repeat the operation and predictably produce a product which meets the original specifications. Such time-cycle control has been utilized to produce a high-quality, polycyclic hydrocarbon material from the previously discussed light cycle oils. This desirable desorbate was produced at a nominal 4 gallons per minute per square foot feed rate and by initially utilizing a 1.58 refractive index cut point for the second phase of the recycle stream. When operating in this manner, the desorbate product has a refractive index of 1.59, contains 80 to 88% polycyclic hydrocarbons and a 35% yield of desorbate is produced. Table X illustrates runs made in this fashion.

TABLE X

	1	2	3	4	5
Recycle feed, wt. lbs	123	104.5	104.5	102.5	100.0
Fresh feed, wt. lbs	4	12.5	15.0	17.5	16.5
Total feed, wt. lbs	127	117.0	119.5	120.0	116.0
Total cycle time, sec	5,350	5,200	5,200	5,150	5,300
Raffinate, wt. lbs	15.7	8.7	9.3	10.6	9.1
Yield, percent	82.6	67.4	68.4	71.6	65.5
Cut Point RI	1.5070	(1)	1.4950	1.5070	1.4980
Raffinate RI	1.4830	1.4865	1.4770	1.4780	1.4750
CS_2 in Raff., percent	75.1	82.1	82.1	81.2	82.2
Time, sec	1,200	±1,050	1,000	1,050	1,050
Recycle, wt. lbs	106.5	108	105.5	103.5	99.5
Cut Point RI	1.5840	1.5825	1.5800	1.5760	1.5710
Recycle RI	1.5275	1.524	1.5250	1.5215	1.5250
Time, sec	2,300	2,300	2,300	2,300	2,300
CS_2 wash period, sec	400	400	400	400	500
Desorbate, wt. lbs	3.3	4.2	4.3	4.2	4.8
Yield, percent	17.4	32.6	31.6	28.4	34.5
Desorbate RI	1.5960	1.5930	1.5940	1.5900	1.5860
Naph.-ace. percent	88.02	86.27	86.35	85.7	79.2
CS_2 wt. percent desorbate	96.6	96.1	96	96	95.5

[1] Valve trouble.

Table XI compares adsorption products having 80% and 88%, respectively, of naphthalene-acenaphthene with the light cycle oil feed utilized in these runs.

TABLE XI

Characterization of Products

	Pilot plant feed	80% polycyclics	88% polycyclics
Gravity	21	11.1	9.4
Distillation:			
IBP	435	456	
5	450	460	470
10	454	460	474
20	459	468	478
30	462	470	479
40	465	472	481
50	469	474	482
60	472	476	484
70	475	479	487
80	479	483	490
90	484	490	494
95	489	496	498
EP	490	502	504
Chromatographs:			
<Naphthalene	62.2	9.10	4.4
Naph.-ace	24.2	82.95	88.14
>Ace	13.6	7.95	7.46

Table XII illustrates the effectiveness of time-cycle control in producing polycyclic products from a light cycle oil. By altering the time-cycle, products containing anywhere from 50% to 88% naphthalene-acenaphthene can be readily produced and of greater significance is the fact that a given product can be repeatedly produced from the same feed by utilizing the same time cycle.

It is obvious from Table XII that the first portion of the recycle can be introduced in anywhere from 1450 to 1600, the second portion of recycle from 100 to 500 seconds, fresh feed from 500 to 900 seconds, the first portion of carbon disulfide from 2000 to 2300 seconds, and the second portion of carbon disulfide from 500 to 1200 seconds; and the total cyclic operation may vary from 5250 to 5800 seconds. This particular time cycle is for a column having a height of 22 feet and a nominal diameter of 4 inches, or 0.088 square feet in cross section, and utilizing a 4-gallon per minute per square foot feed rate. Obviously for other size columns, the time cycle will differ. However, the important point is that once a time cycle has been established by utilizing product quality as a measure, whether this be by refractive index measurements or some other means, the time cycle can then be utilized to carry out the operation and repeatedly produce products meeting the initial specifications. The cycle would, of course, change if a radical change in the composition of the feed occurred. However, under normal operating conditions, this will not be the case and the time cycle would normally be reset if a change in feed was made.

TABLE XII

Time Cycle and Yields for Various Polycyclic Products

Feed	Effluent	Typical 50% naph.-ace. Time	Typical 50% naph.-ace. Total	Typical 60% naph.-ace. Time	Typical 60% naph.-ace. Total	Typical 80% naph.-ace. Time	Typical 80% naph.-ace. Total	Typical 88% naph.-ace. Time	Typical 88% naph.-ace. Total
Recycle	Desorbate	1,600	1,600	1,500	1,500	1,450	1,450	1,450	1,450
	Raffinate	100	1,700	400	1,900	550	2,000	500	1,950
Fresh feed	Raffinate	900	2,600	800	2,700	500	2,500	500	2,450
CS_2	Recycle	2,000	4,600	2,100	4,800	2,300	4,800	2,300	4,750
	Desorbate	1,200	5,800	1,000	5,800	500	5,300	500	5,250
Pounds of desorbate		16		11.5		4.8		4.33	
Pounds of naph.-ace		8.2		6.8		3.8		3.72	
Carbon effectiveness, pounds carbon required per pound of Hydeal feed		5.8		7.1		12.6		12.9	

Finally, Table XIII shows a comparison of a polycyclic product produced from light cycle oil in accordance with the present invention as compared with three commercially available materials which are sold for the production of naphthalene from polycyclic hydrocarbon concentrates.

TABLE XIII

Constituents	Present process	Commercial A	Commercial B	Commercial C
<Naphthalene	0.52	9.1	13.8	3.7
Naphthalene	0.95	26.9	17.8	13.6
5-methyltetralin		6.3	7.5	3.0
Naph.-ace	92.49	49.90	55.00	74.10
>Acenaphthene	0.92	4.2	5.8	4.3
Unidentified	5.12	3.6	0.3	1.3

Where the term "more readily adsorbed" components is used herein, it is meant to refer to the component or components of a multi-component mixture which the carbon will preferentially adsorb from the mixture to the exclusion of the "less readily adsorbed" components which will pass through the carbon without being adsorbed to any great extent. For example, the following order of adsorptive preference is recognized in the art for carbon, polycyclics>, monocyclics>, linear hydrocarbons, having refractive indices of greater than about 1.550, between about 1.550 and 1.480, and less than 1.480, respectively.

We claim:

1. A method for separatnig hydrocarbon mixtures; comprising, contacting said hydrocarbon mixture with activated carbon to selectively adsorb on said carbon a more readily adsorbed fraction of said hydrocarbon mixture and leave unadsorbed a less readily adsorbed fraction of said hydrocarbon mixture, and removing said selectively adsorbed hydrocarbon fraction from said carbon by passing carbon disulfide into said carbon.

2. A method in accordance with claim 1 wherein the hydrocarbon mixture contains cyclic and non-cyclic hydrocarbons and said cyclic hydrocarbons are selectively adsorbed.

3. A method in accordance with claim 1 wherein the hydrocarbon mixture contains polycyclic aromatic hydrocarbons, monocyclic aromatic hydrocarbons and aliphatic hydrocarbons and said polycyclic aromatic hydrocarbons are selectively adsorbed.

4. A method in accordance with claim 3 wherein the hydrocarbon mixture is a light cycle oil obtained from a catalytic cracking operation.

5. A method in accordance with claim 1 wherein a preselected portion of the effluent from the adsorption-displacement operation is recycled to the adsorption column.

6. A method in accordance with claim 1 wherein a predetermined volume of carbon disulfide is utilized as a displacing fluid.

7. A method in accordance with claim 1 wherein the adsorption-displacement is carried out utilizing a multiphase cyclic operation of a fixed bed of carbon.

8. A method in accordance with claim 7 wherein the cyclic operation is controlled by observing the refractive index of at least one predetermined stream and adjusting the operation as needed.

9. A method in accordance with claim 8 wherein the cyclic operation comprises passing the hydrocarbon mixture through the carbon and discharging an effluent comprising raffinate and carbon disulfide; passing a first portion of carbon disulfide through said carbon and collecting an effluent comprising a recycle mixture; passing a second portion of carbon disulfide through said carbon and collecting an effluent comprising adsorbate and carbon disulfide; passing a first portion of said recycle mixture through said carbon while continuing to collect an effluent comprising adsorbate and carbon disulfide, and passing the remaining portion of said recycle mixture through said column and collecting an additional portion of effluent comprising raffinate and carbon disulfide.

10. A method in accordance with claim 9 wherein the hydrocarbon mixture is passed through the bed of carbon until the raffinate has a first, predetermined refractive index.

11. A method in accordance with claim 9 wherein the first portion of carbon disulfide is passed through the carbon until the recycle has a second, predetermined refractive index higher than the first refractive index.

12. A method in accordance with claim 9 wherein collection of adsorbate-carbon disulfide mixture is discontinued when all of a predetermined volume of carbon disulfide has been utilized.

13. A method in accordance with claim 9 wherein collection of the adsorbate-carbon disulfide mixture is discontinued when said adsorbate reaches a third, predetermined refractive index lower than the second refractive index.

14. A method in accordance with claim 9 wherein the collection of the additional portion of raffinate is discontinued when all of the collected recycle effluent has been used.

15. A method in accordance with claim 8 wherein the cyclic operation is controlled by utilizing a predetermined time of operation for each phase.

16. A method in accordance with claim 15 wherein the predetermined times are established by observing the refractive index of at least one predetermined stream, simultaneously measuring the time of operation for each phase and selecting the times at which the refractive index is a predetermined value.

17. A method of separating a mixture of cyclic and non-cyclic hydrocarbons comprising passing said mixture into and through activated carbon to adsorb thereon a mainly cyclic fraction of said mixture having a refractive index of at least about 1.45 and leaving unadsorbed a mainly non-cyclic fraction of said mixture having a refractive index of no greater than about 1.45, and removing the adsorbed fraction by passing carbon disulfide into and through the activated carbon.

18. A method in accordance with claim 17 including recycling a first portion of the adsorbed fraction, said first portion having a refractive index of no greater than about 1.59.

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U.S. Cl. X.R.

260—666 SA, 674 SA, 674 N, 708