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D. B. CARPENTER ET AL

3,697,414

METHOD FOR PRODUCING NAPHTHALENE

Filed April 5, 1971

2 Sheets-Sheet 1

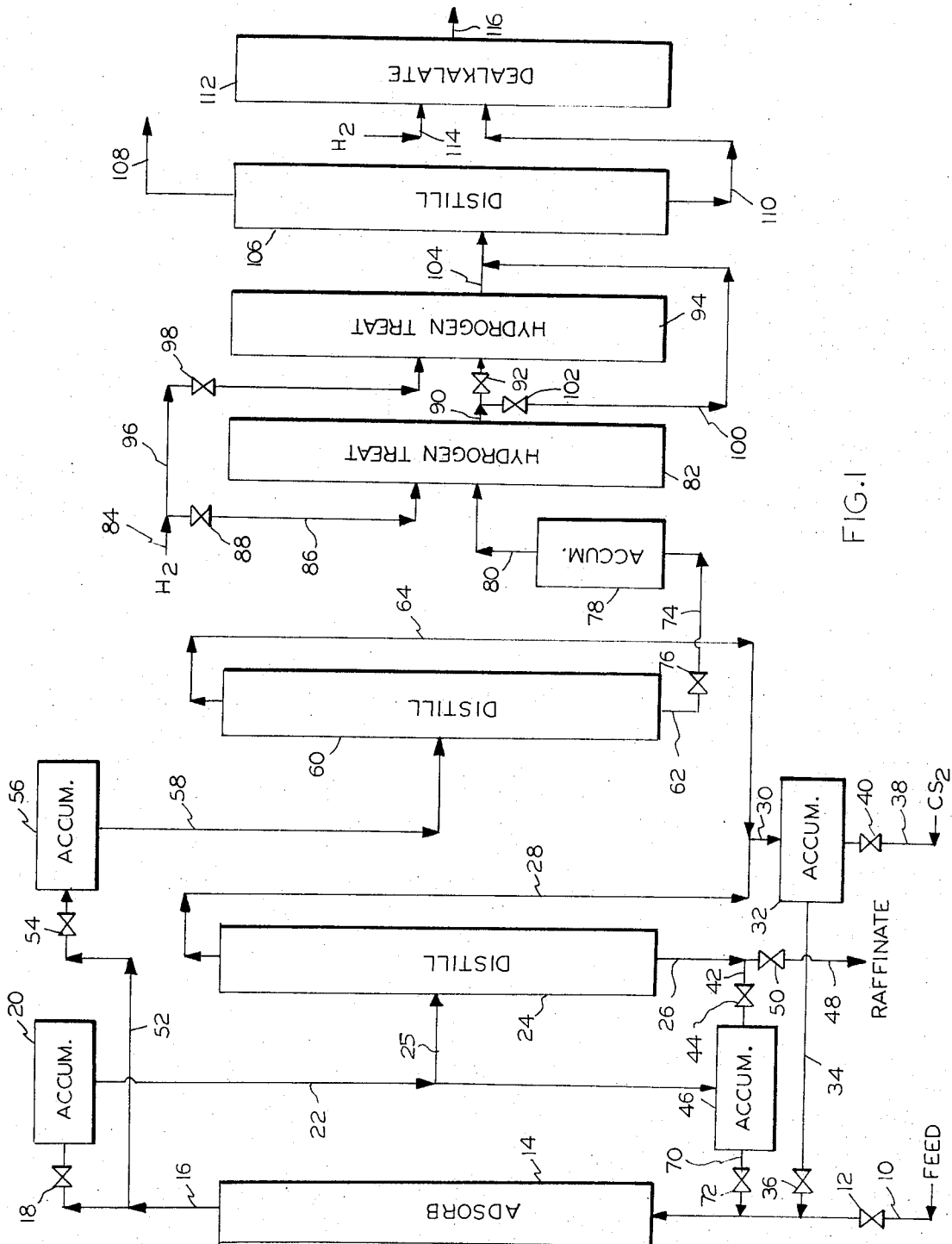


FIG. 1

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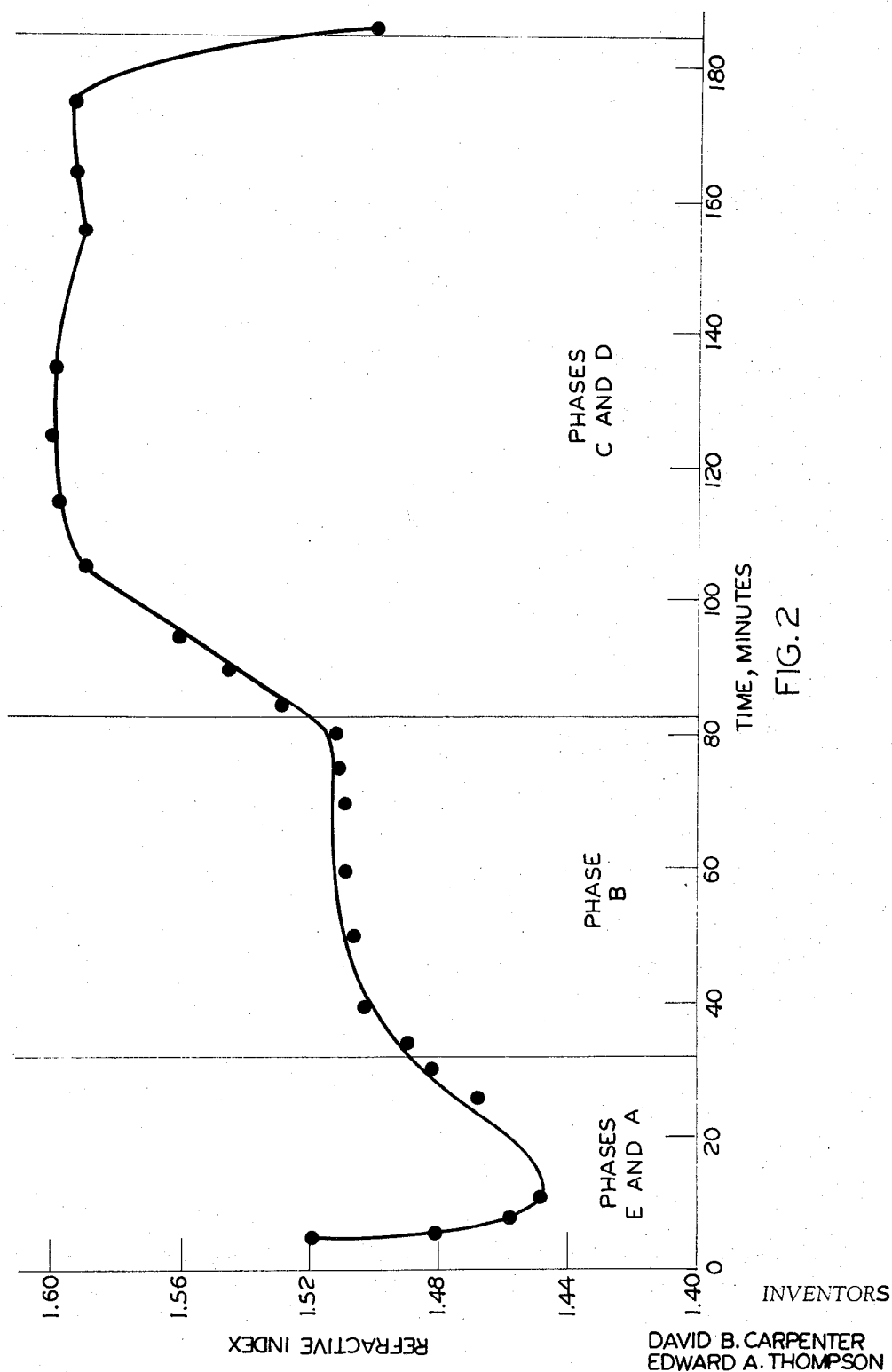


FIG. 2

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METHOD FOR PRODUCING NAPHTHALENE

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18 Claims

ABSTRACT OF THE DISCLOSURE

Hydrocarbon mixtures, such as light cycle oils from a catalytic cracking unit, are selectively separated by a cyclic adsorption technique involving passing the hydrocarbon mixture through a fixed bed of activated carbon to adsorb selectively polycyclic aromatic components as an adsorbate phase while collecting less readily adsorbed components as 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; separating carbon disulfide from the raffinate and adsorbate phase for reuse as a displacing fluid; passing the adsorbate to at least one hydrogen treating operation under conditions such that residual aliphatic hydrocarbons are cracked, residual alkyl monocyclic hydrocarbons are dealkylated, polycyclic aromatics remain unreacted and the mixture is desulfurized, separating the hydrogen-treated product into a light fraction and a heavy fraction and subjecting the heavy fraction to a hydrodealkylation treatment to produce substantial volumes of naphthalene.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to the production of naphthalene from a light cycle oil of a catalytic cracking operation by contacting the cycle oil with activated carbon to selectively adsorb the polycyclic aromatics; thereafter displacing the polycyclic aromatics with carbon disulfide; and subjecting the desorbed polycyclic aromatics to hydrodealkylation.

Description of the prior art

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 primarily 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 of coal tars, particularly since the major por-

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tion 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 naphthalenes and alkyl-substituted naphthalenes and only minor quantities of monocyclic aromatics and paraffins. These feeds may, therefore, be directly processed in a hydrodealkylation unit 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 directly hydrodealkylate this material since the consumption of hydrogen is extremely high, substantial quantities of valuable hydrocarbons are downgraded to fuel gas, and hydrogen to hydrocarbon mole ratios must be maintained at extremely high levels to prevent excessive reactor temperatures and rapid coke laydown.

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. Further concentration of polycyclics should also include a reduction of the sulfur content of the hydrocarbon mixture, since hydrocarbon mixtures of the character referred to herein normally contain substantial quantities of sulfur compounds and such sulfur compounds are detrimental to further reactions of the concentrated polycyclic materials.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide an improved method for the production of naphthalene. Another object of the present invention is to provide an improved method for the production of naphthalene from petroleum hydrocarbon mixtures. A still further object of the present invention is to provide an improved

method for the production of naphthalene 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 naphthalene by passing a petroleum hydrocarbon mixture containing paraffins, monocyclic aromatics, and dicyclic aromatics, through an adsorbent to separate dicyclic aromatics therefrom and thereafter subjecting the dicyclic aromatic adsorbate to catalytic hydrodealkylation. A still further object of the present invention is to provide an improved method for the production of naphthalene wherein a catalytic light cycle 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, the displacing fluid is recycled to the adsorption step and the adsorbate is subjected to catalytic hydrodealkylation. Another and further object of the present invention is to provide an improved technique for the concentration of polycyclic aromatics from a mixture of polycyclic aromatics, monocyclic aromatics and paraffins; including, separating the polycyclics by adsorption, subjecting the mixture to a hydrogen treatment under conditions to convert the paraffins to lower boiling paraffins, convert the monocyclic aromatics to lower boiling monocyclic aromatics, and leave unaltered the polycyclic aromatics; separating the polycyclic aromatics from the remaining materials; and subjecting the polycyclic aromatics to a hydrodealkylation treatment.

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 by selectively adsorbing polycyclic aromatics on activated carbon; passing carbon disulfide through the activated carbon containing the selectively adsorbed adsorbate to displace the same; recovering the displaced adsorbate; and subjecting the adsorbate to a hydrodealkylation treatment to produce substantial volumes of naphthalene.

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 adsorption 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 now 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 start-up 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 dicyclic hydrocarbons, the raffinate phase will be the less desirable monocyclic and paraffinic materials. 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 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 70 and valve 72 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

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in distillation column 24. The raffinate is then treated as previously described.

The adsorbate or selectively adsorbed material contains substantial volumes of polycyclic and higher hydrocarbons, whereas the raffinate or non-adsorbed phase is primarily aliphatic and monocyclic hydrocarbons. The adsorbate is then further treated by passing the same through line 74 and valve 76 to accumulator 78. From accumulator 78, the adsorbate passes to line 80 to hydrogen treating unit 82. Hydrogen treating unit 82 is supplied with hydrogen through hydrogen supply line 84, line 86 and valve 88. The product of hydrogen treater 82 is generally passed through line 90 and valve 92 to a second hydrogen treating unit 94. Hydrogen treater 94 is supplied with hydrogen from supply line 84 through line 96 and valve 98. In the preferred operation, hydrogen treater 82 is a hydrodesulfurization unit, whereas hydrogen treater 94 is a hydrocracking-hydrodealkylation unit. The operation of these units and their purposes will be discussed hereinafter in greater detail. In the alternative, hydrogen treater 82 may be operated as a hydrocracker-hydrodealkylator and hydrogen treater 94 may be utilized as a hydrodesulfurization unit. In still another variation, a single hydrogen treating unit may be employed, such as unit 82, which would be operated as a hydrocracker-hydrodealkylation unit since an operation of this type does accomplish a certain amount of desulfurization. In this last instance, the product from hydrogen treater 82 would pass through line 100 and valve 102, thereby bypassing the second hydrogen treater 94. Either the product from hydrogen treater 82, passing through line 100, or the product of hydrogen treater 94, passing line 104, is then charged to distillation unit 106. In distillation unit 106, the product is separated into an overhead product, which is discharged through line 108 and a bottoms product, which is discharged through line 110. The overhead fraction will generally comprise hydrocracked paraffins and dealkylated monocyclic aromatics whose boiling points have been lowered by the hydrocracking-hydrodealkylation treatment and which will then boil below the desired polycyclic materials. In some cases the hydrogen treater may be eliminated. The desired polycyclic material may then be discharged through line 110 to hydrodealkylation unit 112. Hydrodealkylation unit 112 is supplied with hydrogen through line 114 and the products of hydrodealkylation unit 112 are discharged through line 116. The overhead product of line 108 generally is a material boiling in the gasoline boiling range and is a suitable gasoline blending stock. Accordingly, it would be passed to gasoline storage or a gasoline treating plant.

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
Void in dense packed column, percent -----	20-50
Specific heat at 100° C. -----	0.2-0.3

¹ Brunauer, Emmitt 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

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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):	
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
Void in dense packed column, percent -----	44
Specific heat at 100° C. -----	0.25

¹ Brunauer, Emmitt 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:	
Flash, ° F. -----	220
Fire, ° F. -----	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 to be a worthwhile feed material for a hydrodealkylation operation or other operation for the recovery of aromatics since polycyclic concentrates for such use 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 stream after carbon disulfide has been removed therefrom.

TABLE III.—STEAM STRIPPING CARBON

Cycle	1	2	4	5
Charge:				
Refractive index	1.5163	1.5163		
Weight, gms.	2,504	2,340	1,968	2,220
Pumped	1,130	1,248	851	1,154
Blowdown	696	526	797	780
Grams adsorbed (by diff.)	678	566	320	286
Recovery	548		261	227
Loss	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 naphthalene precursors 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 high refractive index materials. This higher yield of the high refractive index materials is a function of the higher equilibrium capacity of the carbon, the ability of the carbon disulfide to effectively displace these higher refractive index materials, and the higher selectivity for high refractive index materials which the carbon disulfide imparts to the carbon.

TABLE IV.—CARBON DISULFIDE DISPLACEMENT

Cycle	1	2	3	4	5	6
Charge:						
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
Grams total raffinate	1,548	1,919	1,971	1,992	1,994	2,010
Grams "Adsorbate"	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's.	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.

ADSORBATE QUALITY
(Table III Runs) (Table IV Runs)

	Feed	Steam stripped adsorbate	CS ₂ stripped adsorbate		
			Cycle 1	Cycle 2	Cycle 3
Gas chromatograph:					
BMN	51.0	47.0	40.9	41.7	41.7
BMN	9.6	9.4	8.2	7.4	7.2
AMN		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

Table V below summarizes the results of hydrotreating the adsorbate of the last run and thereafter hydrodealkylating a bottoms product of the hydrotreating.

TABLE V

Hydrotreating of adsorbate

WHSV	1.0
Temperature, ° F.	1025
Pressure, p.s.i.g.	1000
H ₂ /HC	7/1
Liquid yield, wt. percent	62.5
Liquid product distillation, vol. percent:	
Gasoline	31.2
Hydeal feedstock	68.8

Dealkylation of 400° F.+hydrotreated bottoms

Dealkylation:

WHSV	1.0
Temperature, ° F.	1325
Pressure, p.s.i.g.	400
H ₂ /HC	15/1
Liquid yield, percent	81.2

10 Product analysis, percent:

B	2.5
T	4.6
X	2.5
X-N	3.7
N	69.6
N-MN	
MN	15.9
DMN+Biph	0.9
Ace+>	0.4
Potential benzene, percent	6.7
Potential naphthalene, percent	68.1

A series of runs was also made in order to determine whether benzene could be utilized as a desorption 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 VI 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 VI 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.

TABLE VI

40 Fresh feed, gms.	579
Fresh feed, cc.	640
Recycle feed, gms.	772
Recycle feed, cc.	860
Raffinate:	
45 Weight, gms.	199
Final RI	1.489
Average RI	1.476
Naphthalene precursors, percent	5.2
Yield, wt. percent	36.3
50 Recycle:	
Weight, gms.	807
Volume, cc.	900
Initial RI	1.489
Final RI	1.520
Average RI	1.512
Adsorbate:	
60 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
65 Cycle time, minutes	255
Adsorption rate, cc./min.	11.5
Desorption rate, cc./min.	23.0
Vol. CS ₂ , cc.	3,000
70 No blowdown after adsorption.	
Blowdown after desorption.	

Table VII shows the results of hydrotreating and thereafter dealkylating the adsorbate obtained from the run of Table VI.

TABLE VII.—DOWNSTREAM PROCESSING OF ADSORBATE¹

Hydrotreating:	
Conditions:	
Temperature, ° F.....	1,000
Pressure, p.s.i.g.....	1,000
Hydrogen rate, s.c.f./bbl.....	12,000
WHSV.....	1.0
Hydrogen consumption, s.c.f./bbl.....	1,250
Yield of liquid, weight percent.....	83
	Wt. percent Vol. percent
Fractionation:	
Total liquid.....	100 100
Gasoline, 400° F.....	28.4 31.7
Hydeal feedstock, 400° F.....	71.6 68.3
Dealkylation, 400° F.,+ bottoms:	
Hydeal Feed, weight percent.....	100
Benzene, weight percent.....	6.5
Naphthalene, weight percent.....	64.9
Yield on LCO, weight percent.....	24.6

¹ Contains ~ 5.1% N-Ace.

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 VIII below illustrates the general character of this five-phase operation.

TABLE VIII

Phase	In	Out	Valves open	Termination of phase
A.....	Feed.....	Raffinate plus 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 plus 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 plus 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 VIII 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 VIII, 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 non-adsorbed 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. 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 IX below summarizes an optimum treatment of light cycle oil feed when carried out in the five-phase cyclic manner set forth in Table VIII.

TABLE IX

Fresh feed, gms.	533
Fresh feed, cc.	595
Recycle feed, gms.	854
Recycle feed, cc.	950
Raffinate:	
Weight, gms.	217
Final RI	1.495
Average RI	1.475
Recycle:	
Weight, gms.	872
Volume, cc.	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, cc./min.	23.0
Desorption rate, cc./min.	23.0
CS ₂ vol., cc.	2000
No blowdown after adsorption.	
No blowdown after desorption.	

Table X shows the results of directly dealkylating the adsorbate of the run of Table IX.

TABLE X

Dealkylation of adsorbate	
Adsorbate:	
Naphthalene precursors, percent	56
Wt. yield, percent	100
Naphthalene, percent	43-46
Yield on LCO	25.0-26.8

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The first column of Table XI 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 XI 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 XI

Fresh feed, gms.....	867	859
Fresh feed, cc's.....	940	960
Recycle feed, gms.....	420	460
Recycle feed, cc's.....	470	505
Column length, feet.....	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.....	1.515	1.515
Blowdown used		
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's.....	3,000	3,000
Cycle time, min.....	370	212
Desorption rate, cc's./min.....	11.5	22
Adsorption rate, cc's./min.....	11.5	22

The only limitations on the type of material treated in the adsorption column 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. The adsorption 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 both feed and displacing fluid 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. The recycle rate is preferably 3.5 to 5.0. 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 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 such high carbon disulfide ratios also require increased capital investment due to the fact that the carbon disulfide is toxic and explosive.

The first hydrogen treating operation may be carried out under conventional conditions and utilizing conventional hydrodesulfurization catalysts. For example, the temperature may be between about 400 and 1000° F., at a pressure of about 50 to 2000 p.s.i.g., and a liquid hourly space velocity between about 0.1 and 20, and hydro-

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gen rate between about 500 and 15,000 standard cubic feet per barrel of feed may be employed. Also, a wide variety of catalysts may be utilized. Preferably, any hydrogenation metal on an inert oxide carrier may be utilized. For example, platinum, nickel, cobalt, molybdenum, tungsten, and mixtures of these materials on alumina, silica, or silica-alumina carriers may be utilized. The hydrocracking-hydrodealkylation catalysts hereinafter mentioned may also be utilized in the hydrodesulfurization step under hydrodesulfurization conditions.

The second hydrogen treating operation is carried out in the presence of a cracking catalyst. Catalysts of this nature containing a Group VIII metal alone or in combination with other metals have been found most outstanding. It has been found that under the conditions set forth herein and when utilizing nickel- or cobalt-containing catalysts, excellent results can be obtained in the concentration of polycyclic aromatics from mixtures containing such polycyclic aromatics, paraffins, and monocyclic aromatics boiling in essentially the same boiling range.

The nickel content of the catalyst may vary between about 1 and 60% by weight of the total catalyst, and the nickel may be combined with other metals. By far the most effective catalyst in accordance with the present invention is one containing about 3% nickel and about 3 to 15% molybdenum, deposited on an alumina carrier. The combinations of nickel, molybdenum and cobalt on activated alumina have also been found effective. Catalysts containing 4% nickel, and 16% tungsten on alumina, 58% nickel on kieselguhr, and a coprecipitate of 60% nickel, as nickel oxide, and alumina have also been found useful. However, none of the latter appear the equal of the first mentioned nickel-molybdenum catalyst. Cobalt, in essentially the same concentrations, can be substituted for nickel in the catalyst system. A particularly effective catalyst for the present purpose is a catalyst containing about 3.5% cobalt oxide and 12.5% molybdenum oxide deposited on an alumina carrier. A similar catalyst can also be formed by depositing the cobalt and molybdenum on a silica-alumina base having a ratio of silica/alumina of 3/1.

The operating conditions of the second hydrogen treating operation are also important to the polycyclic aromatic concentration. Specifically, the temperature should be between about 800 and 1200° F. and, preferably between about 850 and 1050° F. A pressure between about 250 and 5000 p.s.i.g., and preferably above 1000 p.s.i.g., is preferred. The space velocity should be between about 0.2 and 5, and, preferably between about 0.5 and 2. Finally, the hydrogen rate should be between about 2000 and 20,000 standard cubic feet per barrel of feed, and, preferably between 2,000 and 15,000 standard cubic feet per barrel.

The hydrodealkylation unit may be operated under conventional hydrodealkylation conditions and utilizing conventional hydrodealkylation catalysts. A highly effective catalyst for this purpose is chromium on alumina. Suitable operating conditions include a temperature between 900 and 1400° F., and a pressure between 100 and 1000 p.s.i.g. However, for best results, in the conversion of alkyl polycyclic aromatics to naphthalene, the temperature should be 1200° F. at the entrance to the dealkylation unit and 1350° F. at the exit. The pressure should preferably be between about 150 and 750 p.s.i.g. As previously indicated, the second hydrogen treating operation selectively cracks paraffins and removes (dealkylates) and cracks side chains from mononuclear aromatics without affecting the aromatic ring. In conventional hydrocracking operations, aromatics are partially or completely hydrogenated to naphthenes and the partially saturated aromatics and naphthenes are then cracked to break the ring. In the present invention, the catalyst and conditions are selected so that this normal production of naphthenes and ring destruction is avoided.

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 sq. 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 of 1.59, contains 80 to 88% polycyclic hydrocarbons and a 34% yield of desorbate is produced. Table XII illustrates runs made in this fashion.

TABLE XII

	1	2	3	4	5
Recycle feed, wt. lbs.	123	104.5	104.5	102.5	100
Fresh feed, wt. lbs.	4	12.5	15	17.5	16.5
Total feed, wt. lbs.	127	117	119.5	120	116
Total cycle time, seconds	5,850	5,200	5,200	5,150	5,800
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, seconds	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, seconds	2,300	2,300	2,300	2,300	2,300
CS ₂ wash period, seconds	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	86.37	86.35	85.7	79.2
CS ₂ , wt. percent/desorbate	96.6	96.1	96	96	95.5

1 Valve trouble.

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

TABLE XIII.—CHARACTERIZATION OF FEEDSTOCKS

	Feed		
	Pilot plant	80% Hydeal	88% Hydeal
Gravity	21	11.1	9.4
Distillation:			
IBP	435	456	470
5	450	480	474
10	454	468	478
20	459	470	479
30	462	472	481
40	465	474	482
50	469	476	484
60	472	479	487
70	475	483	490
80	479	490	494
90	484	496	498
95	489	502	504
EP	490		
Chromatographs:			
<Naphthalene	62.2	9.10	4.4
Naph.-Ace	24.2	82.95	88.14
>Ace	13.6	7.95	7.46

Table XIV illustrates the effectiveness of time-cycle control in producing polycyclic products from a light cycle oil. It is obvious that 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, utilizing the same time cycle.

It is obvious from Table XIV 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 XIV.—TIME CYCLE AND YIELDS FOR VARIOUS HYDEAL FEED STOCKS

Feed	Effluent	Typical 50% Naph.-Ace.		Typical 60% Naph.-Ace.		Typical 80% Naph.-Ace.		Typical 88% Naph.-Ace.	
		Time	Total	Time	Total	Time	Total	Time	Total
Recycle	Desorbate	1,600	1,600	1,500	1,500	1,450	1,450	1,450	1,450
Do	Raffinate	100	1,700	400	1,900	550	2,000	500	1,950
Fresh Feed	Raffinate	900	2,600	800	2,700	600	2,600	500	2,450
CS ₂	Recycle	2,000	4,600	2,100	4,800	2,300	4,800	2,300	4,750
CS ₂	Desorbate	1,200	5,800	1,000	5,800	600	5,300	500	5,250
Pounds of desorbate		16		11.5		4.8		4.38	
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	

Table XV 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 XV

Constituents	Present process	Commercial		
		A	B	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

Finally, Table XVI illustrates the results obtained by processing various desorbates produced in the present manner without hydrotreating the adsorbate. The 55% naphthene-acenaphthene desorbate is presented for comparative purposes.

TABLE XVI.—DEALKYLATION OF DESORBATE

	Percent		
	55% Naph-Ace	88% Naph-Ace	80% Naph-Ace
Heart cut LCO.....	24	24	24
Desorbate Naph-Ace.....	54	88	82
Yield of desorbate.....	51.6	133.9	34.5
Naphthalene potential.....	49	68.7	62.5
Yield on LCO.....	25.3	23.3	21.9
Naphthalene potential by dealkylation.....	28.4	28.4	28.4
Naphthalene recovery.....	89	82	77.1

† Yield figures from typical equilibrated run.

‡ Reflects loss of precursors to raffinate. This can be corrected.

We claim:

1. A method for producing naphthalene from a hydrocarbon mixture containing polycyclic aromatic hydrocarbons, monocyclic aromatic hydrocarbons and aliphatic hydrocarbons; comprising, contacting said hydrocarbon mixture with activated carbon to selectively adsorb on said carbon said polycyclic aromatic hydrocarbons and leave unadsorbed said monocyclic aromatic hydrocarbons and said aliphatic hydrocarbons; removing said adsorbed polycyclic aromatic hydrocarbons from said carbon by passing carbon disulfide into said carbon; and subjecting said removed polycyclic aromatic hydrocarbons to hydrodealkylation.

2. A method in accordance with claim 1 wherein the hydrocarbon mixture is a light cycle oil obtained from a catalytic cracking operation.

3. A method in accordance with claim 1 wherein the removed polycyclic aromatic hydrocarbons are subjected to at least one hydrogen treatment under conditions to dealkylate residual monocyclic aromatic hydrocarbons and crack residual aliphatic hydrocarbons.

4. A method in accordance with claim 3 wherein the product of the hydrogen treatment is separated into a low boiling fraction and a high boiling fraction and said high boiling fraction is subjected to the hydrodealkylation treatment.

5. A method in accordance with claim 3 wherein a second hydrogen treatment is carried out under conditions to desulfurize the product of the first hydrogen treatment.

6. A method in accordance with claim 5 wherein the product of the second hydrogen treatment is separated into a low boiling fraction and a high boiling fraction and said high boiling fraction is subjected to the hydrodealkylation treatment.

7. A method in accordance with claim 1 wherein a pre-

selected portion of the effluent from the adsorption-displacement operation is recycled to the adsorption column.

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

9. 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.

10. A method in accordance with claim 9 wherein the cyclic operation is controlled by observing the refractive index of at least one predetermined stream and adjusting the operation as needed.

11. A method in accordance with claim 9 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; passing the remaining portion of said recycle mixture through said carbon and collecting an additional portion of effluent comprising raffinate and carbon disulfide.

12. A method in accordance with claim 11 wherein the hydrocarbon mixture is passed through the bed of carbon until the raffinate has a first, predetermined refractive index.

13. A method in accordance with claim 11 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.

14. A method in accordance with claim 11 wherein collection of adsorbate-carbon disulfide is discontinued when all of a predetermined volume of carbon disulfide has been utilized.

15. A method in accordance with claim 11 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.

16. A method in accordance with claim 11 wherein the collection of the additional portion of raffinate-carbon disulfide mixture is discontinued when all of the collected recycle mixture has been used.

17. A method in accordance with claim 9 wherein the cyclic operation is controlled by utilizing a predetermined time of operation for each phase.

18. A method in accordance with claim 17 wherein the predetermined times are established by observing the refractive index of at least one predetermined stream while simultaneously measuring the time of operation for each phase and selecting the times at which the refractive index is a predetermined value.

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