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RECOVERY OF PETROLEUM NAPHTHALENE

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FIG. 1.

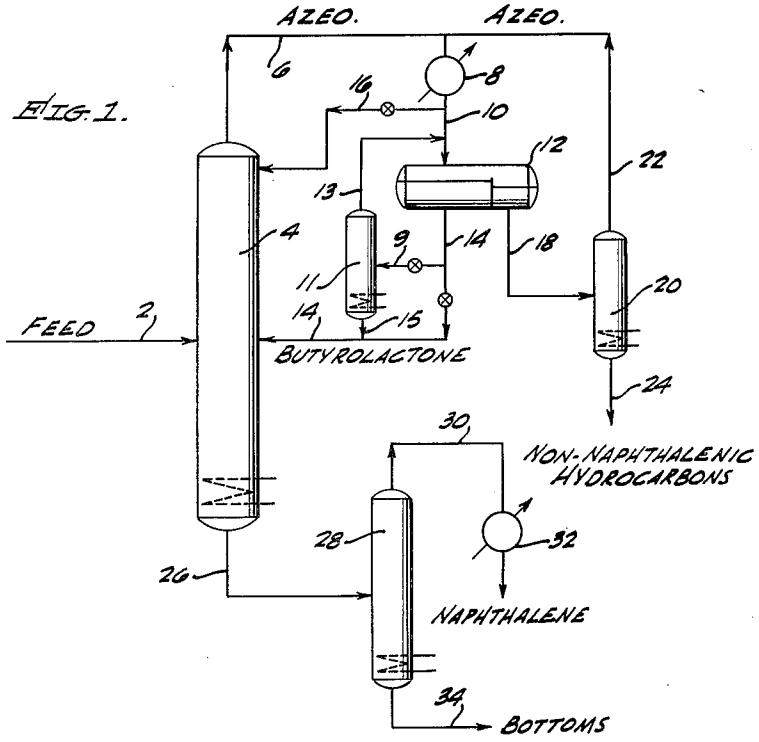
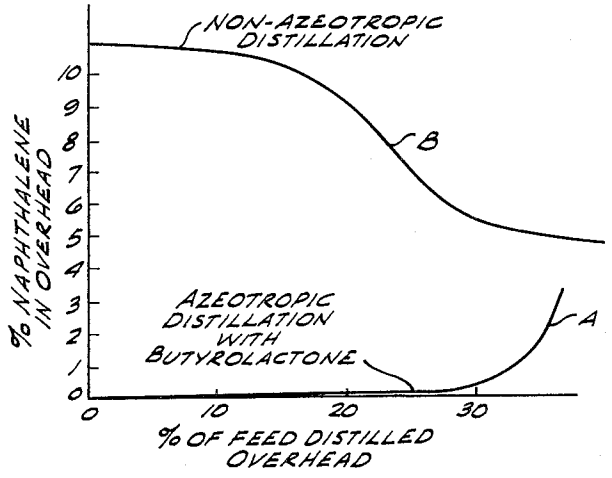


FIG. 2.



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RECOVERY OF PETROLEUM NAPHTHALENE

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This invention relates to new methods for the recovery and purification of naphthalene contained in various hydrocarbon fractions derived from petroleum or the like. More particularly, the method comprises subjecting the hydrocarbon fraction to azeotropic distillation with butyrolactone, whereby non-naphthalenic hydrocarbons boiling in the naphthalene range are azeotroped overhead as a minimum boiling azeotrope with the butyrolactone. It has been found that substantially all of the non-naphthalenic aromatic hydrocarbons contained in these petroleum fractions, and boiling within the 400°–450° F. range, can be efficiently azeotroped out of the mixture before any substantial amounts of naphthalene are distilled overhead. Following removal of the non-naphthalenic hydrocarbons, the naphthalene contained in the remaining bottoms fraction can then be easily recovered by non-azeotropic distillation, or by any other desired means.

It is known that naphthalene fractions containing like-boiling paraffin hydrocarbons can be purified by azeotropic distillation with various azeotroping agents. However, a more difficult problem of separation is involved in this invention, in that the petroleum fractions dealt with are contaminated mainly with aromatic hydrocarbons such as alkyl benzenes, alkyl tetralins, alkyl indanes and the like, boiling within the naphthalene range and thereabouts, e.g., from about 400°–450° F. Petroleum fractions of this nature can be derived from various hydrocarbon conversion and refining processes commonly used in the industry, e.g., catalytic reforming, catalytic cracking, thermal cracking and the like. In particular, catalytic reforming of naphthas produces a heavy reformate fraction boiling above about 400° F., which may contain 40–80% of naphthalene and methyl naphthalenes. The remaining hydrocarbons in this fraction are largely alkyl benzenes, tetralins, indanes and the like. Sometimes a significant proportion of naphthenes are present, but usually little if any paraffins. The recovery of pure naphthalene from such petroleum fractions presents a difficult problem.

Attempts have been made in the past to recover pure naphthalene from such fractions by first subjecting them to catalytic hydrodealkylation to convert the methyl naphthalenes to naphthalene, and then recovering the naphthalene by fractional distillation. None of these methods are entirely satisfactory. In fractional crystallization, eutectics are formed which place severe limitations upon the yields of pure naphthalene which can be recovered. Solvent extraction is difficult and expensive where the contaminants are also mainly aromatic in character. Simple fractional distillation is also impractical because of the close proximity of boiling points of the contaminating hydrocarbons, and also the formation of complex azeotropes. Avoiding these major difficulties, and providing an efficient azeotroping agent for purifying these naphthalene fractions, constitute the principal objects of this invention.

It has now been found that butyrolactone is a remarkably efficient azeotroping agent for separating the non-naphthalenic hydrocarbons in the particular petroleum fractions here concerned. Specifically, it has been found that substantially all of the alkyl benzenes, alkyl tetralins, and alkyl indanes which boil within about 30° F. of naphthalene can be efficiently azeotroped overhead before any substantial amounts of naphthalene appear in the overhead. Moreover, it is found that the azeotropic overhead is unexpectedly rich in hydrocarbons, containing only about 20–50% by weight of butyrolactone, thus minimizing the distillation load, and the amount of azeotroping agent required. Another important advantage resides in the excellent stability of butyrolactone in the system.

Reference is now made to FIGURE 1 of the accompanying drawing, which illustrates schematically one mode of applying the process of this invention. The initial feedstock is brought in through line **2** and admitted to distillation column **4** wherein the primary azeotropic distillation takes place. Column **4** may be a conventional fractional distillation column containing, e.g., 20-80 plates and may be operated at overhead reflux ratios of, e.g., 1:1 to 20:1. Azeotroping is continued until essentially all the non-naphthalenic hydrocarbons boiling within about 10° F., and preferably 20° F., of naphthalene, are distilled overhead. The overhead temperatures during azeotropic distillation will usually range between about 370° and 400° F., butyrolactone itself boiling at 401° F. The azeotropic overhead is taken off through line **6** and condensed in condenser **8**, and the resulting condensate is transferred via line **10** to a liquid-liquid phase separator **12**. To provide the desired reflux ratio, a portion of the condensate in line **10** may be diverted through line **16** and admitted to the top of column **4**.

In phase separator **12**, the condensate may separate spontaneously into two phases, or a small proportion of a miscibility-reducing agent may be required, depending upon the nature of the feed. If the feed is rich in lower alkylated aromatics a miscibility-reducing agent is ordinarily required, but if it is rich in higher alkylated aromatics and/or in naphthenes, adequate phase separation occurs spontaneously. Suitable miscibility-reducing agents include butyrolactone-miscible anti-solvents for hydrocarbons (e.g., water), or hydrocarbon-miscible anti-solvents for butyrolactone, e.g., paraffinic or naphthenic hydrocarbons such as pentane, decane, cyclohexane and the like. Preferably, the miscibility-reducing agent should be easily separable, as by distillation, from the phase in which it is dissolved. Water is ordinarily preferred, and is used in amounts up to about 10% by weight of the butyrolactone, but any small amount is effective in some degree.

The solvent-rich phase which stratifies in separator **12** will ordinarily contain about 1 to 25% of dissolved hydrocarbons, and this solution, if it is free of water, is continuously recycled via line **14** back to a mid-point in distillation column **4**. However, if water is used in separator **12**, the wet solvent is preferably diverted via line **9** to a small distillation column **11**, from which water is distilled overhead via line **13** and returned to separator **12** via line **10**. Water-free solvent is withdrawn as bottoms via line **15** and returned to column **4** via line **14**. The wet butyrolactone can be returned directly to azeotroping column **4**, with some sacrifice of column efficiency.

The hydrocarbon-rich phase in separator **12** ordinarily will contain about 1 to 15% by weight of dissolved butyrolactone. This hydrocarbon-rich phase is then transferred via line **18** to fractionating column **20**, from which all of the butyrolactone is distilled overhead via line **22** as an azeotrope with a portion of the non-naphthalenic hydrocarbons, and condensed into separator **12**. The non-naphthalenic hydrocarbons are withdrawn as bottoms from column **20** via line **24**.

A naphthalene-containing bottoms fraction is continuously withdrawn from azeotroping column **4** via line **26**, and transferred to naphthalene fractionating column **28**. Since all of the close-boiling non-naphthalenic hydrocarbons have been removed in column **4**, the principal separa-

tion which is achieved in column **28** is the separation of naphthalene from methyl naphthalenes. The pure naphthalene overhead is withdrawn via line **30** and condensed in cooler **32** to form pure white naphthalene crystals melting at 80°+ C., and is ordinarily in excess of 99% pure. The methyl naphthalene bottoms from column **28** is withdrawn via line **34** and may be sent to dealkylation facilities not shown to produce additional naphthalene.

The foregoing is not to be considered as limiting the scope of the process. Those skilled in the art will understand that other conventional azeotroping techniques may be employed, and other conventional methods such as fractional crystallization may be employed to recover naphthalene from the azeotroping bottoms.

It is to be noted that butyrolactone also forms an azeotrope with naphthalene, but no difficulty is experienced in obtaining adequate azeotrope fractionation in column **4**, due to the difference in boiling points of the respective azeotropes. If desired, column **28** can also be operated as an azeotropic distillation with butyrolactone, in which case a less efficient column is required since the naphthalene-butyrolactone azeotrope boils lower than naphthalene itself.

The feedstocks which may be treated herein include a wide variety of aromatic petroleum fractions. They may comprise heavy catalytic naphtha fractions, dealkylated light catalytic cycle oils, dealkylated coker distillates, heavy reformate fractions as well as the products of dealkylation thereof, and many similar materials. All of these fractions contain substantial proportions of one or more of the troublesome alkyl benzenes, alkyl tetralins, and alkyl indanes boiling in the 400–450° F. range. They may also contain naphthenes and paraffins, but these contaminants cause no substantial difficulty.

The present invention has particular utility for the treatment of hydrocarbon fractions of the aforesaid types containing naphthalene fractions comprising naphthalene and non-naphthalenic hydrocarbon material boiling within 10° F. thereof, and especially petroleum fractions within the above category in which the naphthalene fraction boils over the entire range of about 410°–450° F. and comprises one or more of the alkyl benzenes, alkyl tetralins and alkyl indanes as the non-naphthalenic hydrocarbon material. More specifically, petroleum fractions within the above class which have been found particularly amenable to treatment by the method of this invention are those boiling above about 400° F. which include, as non-naphthalenic hydrocarbons, alkyl benzenes, alkyl tetralins and alkyl indanes boiling over the entire range of about 414°–434° F.; heavy naphtha reformates boiling above about 400° F. and including a naphthalene fraction boiling over the entire range of about 410°–450° F. which preferably contains alkyl benzenes, alkyl tetralins and alkyl indanes; and heavy naphtha reformates which have been subjected to catalytic hydrodealkylation, boiling over about 400° F. and including a naphthalene fraction boiling over the entire range of about 410°–450° F., which naphthalene fraction perferably contains alkyl benzenes, alkyl tetralins and alkyl indanes.

Ordinarily, it is preferred to remove the light ends from the feed, boiling below about 410° F., since these lighter fractions contain very little naphthalene. The end boiling point of the fraction is not critical herein, but will ordinarily range between about 450° and 600° F.

The dealkylation process referred to herein may consist of any conventional catalytic hydrodealkylation. An especially preferred technique for dealkylating methyl naphthalenes employs steam and hydrogen at elevated temperatures and pressures over a cobalt molybdate catalyst, as is more particularly described in U.S. Patent No. 2,734,929 to Doumani.

The effectiveness of the process is more particularly illustrated in the following examples, which are not however to be construed as limiting in scope.

EXAMPLE I

This example demonstrates the improved recovery of non-naphthalenic hydrocarbons where azeotroping with butyrolactone, as compared to straight fractional distillation. The feed was a blend of platinum reformate ends and catalytic cracked gasoline ends, the blend boiling over the range of about 400°–550° F. (true boiling points). A hydrocarbon type analysis showed the following approximate composition (weight percent):

Paraffins	1.9
Mono-naphthenes	0.8
Poly-naphthenes	1.0
Alkyl benzenes	17.1
Alkyl tetralins + Alkyl indanes	20.0
Naphthalene	6.3
Methyl naphthalenes	46.0
Fluorenes	1.7
Acenaphthene + Biphenyls	3.2

A sample of this feed was subjected to azeotropic distillation with butyrolactone in a 40-plate Oldershaw column at 10:1 reflux ratio, and the naphthalene content of incremental portions of overhead was measured. After 20% of the feed had distilled over, the hydrocarbon component of the overhead still contained less than 0.08% of naphthalene, and even at 30% overhead, the naphthalene content was less than 1%. Curve A of FIGURE 2 shows graphically the very slowly rising naphthalene content of the azeotropic overhead, while Curve B, representing the same distillation carried out in the absence of butyrolactone, shows that the initial overhead contains more than 10% of naphthalene, and none of the first 25% of overhead contained less naphthalene than the feed. It is thus evident that butyrolactone is a remarkably efficient and selective azeotroping agent for this type of feed, while simple fractional distillation is completely impractical.

EXAMPLE II

A. In an attempt to isolate pure naphthalene by simple fractionation from a platinum reformate bottoms fraction which had been subjected to catalytic hydrodealkylation (to convert methyl naphthalenes to naphthalene), 700 grams of the dealkylated product (containing about 39% naphthalene) was subjected to careful fractionation in a 60-plate Oldershaw column at a 20:1 reflux ratio. Twenty-three separate overhead cuts were taken, and the melting points of the richest naphthalene cuts were determined. The results were as follows:

Table 1

Cut	Overhead Temp., ° F.	Wt. of cut, Gms.	Melting Point, ° F.
1–7	270–406	124	
8	421	27.6	
9	424	19.1	156.5
10	426	23.1	169
11	427	24.0	173.5
12	427	29.8	173.5
13	428	37.7	173.5
14	425	19.5	171.0
15	425	26.0	174.0
16	425	18.5	173.0
17	426	19.9	172.0
18	426	18.0	168.0
19	428	18.7	164.0
20	430	9.2	
21	445–466	188.3	
22	468	12.8	
23		80.0	
Botts		11.5	

Since the melting point of pure naphthalene is 179–180° F., it will be apparent that none of the naphthalene cuts taken were more than about 90–95% pure. In order to compare the distribution of hydrocarbon types during distillation, cuts 1–7 were combined into a cumulative frac-

tion A, cuts 8–20 into cumulative fraction B, and cuts 21–23 into cumulative fraction C, and each cumulative fraction was analyzed for the major hydrocarbon types. The results were as follows:

Table 2

	Feed	Composition of Fractions, wt. percent		
		A	B	C
Alkanes				0.2
Mono-naphthenes	0.6	0.2	1.5	0.5
Poly-naphthenes				0.2
Alkyl benzenes	14.0	68.2	4.4	2.1
Tetralins-indanes	10.7	31.6	8.8	7.0
Naphthalene	39.1		85.0	5.9
Methyl naphthalenes	32.0		0.3	75.3
Fluorenes	0.1			0.2

Thus, it is apparent that alkyl benzenes, tetralins, indanes and naphthenes are spread throughout all the fractions, and distillation alone is ineffective for the recovery of pure naphthalene.

B. In contrast to the above, another portion (295 gms.) of the dealkylated feed mixture was blended with 255 gms. of the un-dealkylated feed of Example I, and the blend was fractionated in the same column at a 5:1 reflux ratio, in the presence of 300 gms. of butyrolactone. After 37% by weight of the hydrocarbon feed had been azeotroped overhead (final overhead temperature, 392° F.), the remaining bottoms fraction was washed with water, dried, and subjected to fractional distillation at 5:1 reflux ratio. After discarding a small forerun, eight separate cuts of naphthalene overhead were collected and melting points determined, with the following results:

Table 3

Cut	Overhead Temp., ° F.	Wt. of cut, Gms.	Melting Point, ° F.
1	216.5	11.0	173
2	217	11.0	176.2
3	216.5	6.5	177.0
4	217	17.0	176.2
5	217	14.9	177.5
6	218	13.7	176.4
7	218	15.2	176.5
8	220	10.9	172

Cuts 1–8 represent 99+% pure naphthalene, and since the aggregate amount of these cuts was 100.2 gms., and the feed contained 131 gms. of naphthalene, the yield of this pure naphthalene was over 76.5%.

It will thus be apparent that the process of this invention gives a remarkably efficient recovery of pure naphthalene from the petroleum fractions here concerned. Separations similar to those shown in the examples are achieved when other petroleum fractions within the purview of the invention are employed. The invention is hence not limited to the details of the examples, but only as defined in the following claims:

I claim:

1. A method for the recovery of substantially pure naphthalene from a petroleum fraction boiling above about 400° F., which comprises: (1) subjecting said fraction to azeotropic distillation in admixture with butyrolactone until substantially all the non-naphthalenic hydrocarbons in said fraction which boil within about 10° F. of naphthalene are distilled overhead as an azeotrope with said butyrolactone, and (2) recovering substantially pure naphthalene from the remaining bottoms fraction.

2. A method as defined in claim 1 wherein said non-naphthalenic hydrocarbons comprise at least one hydrocarbon type from the class consisting of alkyl benzenes, alkyl tetralins, and alkyl indanes.

3. A method as defined in claim 1 wherein said non-naphthalenic hydrocarbons include alkyl benzenes, alkyl tetralins and alkyl indanes boiling over the entire range of about 414°–434° F.

4. A method as defined in claim 1 wherein said petroleum fraction is a heavy naphtha reformate including a naphthalene fraction boiling over the entire range of about 410°–450° F.

5. A method as defined in claim 1 wherein said petroleum fraction is a heavy naphtha reformate which has been subjected to catalytic hydrodealkylation, and includes a naphthalene fraction boiling over the entire range of about 410°–450° F.

6. A method for the recovery of substantially pure naphthalene from a petroleum distillate including a naphthalene fraction boiling over the entire range of about 410°–450° F., said naphthalene fraction also containing alkyl benzenes, alkyl tetralins and alkyl indanes, which comprises: (1) subjecting said fraction to azeotropic distillation in admixture with butyrolactone until substantially all the non-naphthalenic hydrocarbons in said fraction which boil within about 20° F. of naphthalene are distilled overhead as an azeotrope with said butyrolactone, and (2) distilling the remaining bottoms fraction in the absence of butyrolactone to recover substantially pure naphthalene overhead.

7. A method as defined in claim 6 wherein said petroleum fraction is a heavy naphtha reformate boiling above about 400° F.

8. A method as defined in claim 6 wherein said petroleum fraction is a heavy naphtha reformate which has been subjected to catalytic hydrodealkylation, and boiling above about 400° F.

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