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2,920,115

PROCESS FOR THE PRODUCTION OF NAPHTHALENE FROM A PETROLEUM OIL

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This invention relates to the production of commercial grade naphthalene from petroleum sources. More specifically, this invention is concerned with the manufacture of commercial grade naphthalene from certain cracked petroleum stocks by a two-stage process including the extraction of the feed stock with a material selective for aromatics and the conversion of the extracted material to naphthalene through the utilization of certain hydroforming catalysts in the presence of hydrogen.

Naphthalene is a highly desirable product which can be derived from petroleum hydrocarbons and many refiners are in search of new methods of producing this material from less desirable charge stocks. The present invention is concerned with a two-stage process for manufacturing naphthalene through extraction of a light cycle oil stock which is usually considered too refractory to be employed as feed in conventional catalytic cracking procedures since the amount of coke formation on the catalysts effected under conditions of cracking is prohibitive. I am aware that the production of naphthalene from cycle oils has been proposed, for instance through utilization of the water-gas reaction or hydropropylolysis. Although these processes may produce desirable amounts of naphthalene other valuable constituents of the charge stock are converted to less valuable products such as gas due to the severe conditions needed to effect the dealkylation of the alkyl naphthalenes in the cycle oils. In the present invention I have devised a method which affords good yields of naphthalene from light cycle oils and at the same time transforms the non-naphthalenic constituents to valuable products.

In the present invention I have found that certain critical process conditions must be observed if the desired result be obtained. First, the selection of the feed stock is most important. My feed is a light cycle oil derived by the catalytic conversion of petroleum hydrocarbon oils through contact with an acidic type catalyst, for instance silica-alumina catalyst. The light cycle oil I employ has a boiling range within about 400° to 600° F. and cycle oils of boiling range within about 450° to 600° F. are preferred. It is important that materials boiling above about 600° F. be excluded from the feed as the high boiling materials such as anthracene and phenanthrene are deleterious to my process. For instance, these materials tend to build up excessively in any recycle stream from the second or hydroconversion stage of my process. It may be desirable in some cases to remove the 400° to 460° F. boiling materials from the light cycle oil feed. However, this cut sometimes contains considerable methyl naphthalenes and methyl tetralins which normally boil higher than 460° F. but distill over at a lower temperature due to azeotropeing.

In the initial stage of my process the feed stock is treated with an extractant such as a solvent or adsorbent which is selective for aromatics. The selection of a suitable extractive material is not critical; however, the degree of extraction effected is of significance. In the extraction I separate a raffinate and an extract phase.

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The raffinate can be discarded from the system and is useful, for instance, as a heating oil or catalytic cracking feed as it is both dearomatized and desulfurized. The extract which is rich in naphthalenics is, after separation from the extractant, passed to the hydroconversion stage of my process. I have found that this extract must have particular characteristics if acceptable yields of naphthalene be produced. The extractive separation must be conducted under conditions such that an extract is afforded which has a refractive index (n_D^{25}) of about 1.55 to 1.61, preferably about 1.57 to 1.61, and a specific dispersion of about 200 to 270 as determined by the blue and green lines of the mercury spectrum. The blue line of the mercury spectrum is called the G-line and has a wave length of 4358 Angstrom units, while the green line of the mercury spectrum is called the E-line and has a wave length of 5461 Angstrom units.

As indicated previously, the selection of an extractive material to afford an extract of the desired properties is not critical. The usual solvents which are selective towards aromatics can be employed. Among these are sulfur dioxide, ethylene glycol-water mixtures, phenol, nitrobenzene, furfural, etc. Likewise the usual adsorbents which are selective for aromatics such as activated silica gel may be employed. It will be apparent that the particular extraction conditions to be observed will vary not only according to whether a solvent or an adsorbent is used, but also according to the particular solvent or adsorbent employed. The conditions necessary to obtain the particular extract desired can be determined by simple experimentation and as an example when using sulfur dioxide as the extractant material the temperature can be about -20 to 20° F., with the sulfur dioxide to oil molar ratio being from about 1:1 to 5:1. Even with this particular solvent the conditions necessary to produce the required extract will vary depending upon the characteristics of the feed within the limits defined.

In the second stage of the present process the aromatic extract oil from the extraction step is treated in the presence of a hydroforming catalyst under severe conditions to ensure the production of (a) sufficient yield of naphthalene in high concentration in its boiling range, (b) conversion of benzenoid aromatics and non-aromatic hydrocarbons to aromatic gasoline, and (c) to effect removal of nitrogen- and sulfur-containing impurities from the desired products. In this stage the reaction conditions are of severity defined by a temperature and space velocity from about 1050 to 1150° F. at 0.5 LHSV (volume of liquid hydrocarbon per hour per volume of catalyst) with various combinations of temperature and space velocity being useable to give a severity in this range, for instance, the operator might employ 1050° F. at 0.5 LHSV or 1400° F. at 8 LHSV in obtaining equivalent severities. The pressure is maintained from at least about atmospheric to 1000 p.s.i.g. or higher and preferably less than 1000 p.s.i.g. The preferred reaction temperature is about 1050° to 1150° F., while the preferred space velocity is about 0.5 to 2 LHSV. Sufficient hydrogen must be present to effect the reaction and maintain the activity of the catalyst through decreasing the amount of coke laydown. The use of about 3 to 10 moles of hydrogen for each mole of feed stock produces satisfactory results and the use of about 5 to 6 moles of hydrogen for each mole of feed is preferred. Of course, the specific amount of hydrogen employed will vary with the feed stock charged and the reaction conditions observed as will the residence time needed to complete the conversion. When operating with recycled tail gases as the hydrogen supply, hydrogen sulfide is preferably removed from the gases.

The catalysts which can be used in the hydroconver-

sion stage of the present process are non-carbon based hydroforming catalysts which can contain chromium, molybdenum, tungsten, cobalt, or vanadium (or mixtures of these) preferably deposited as oxides on non-combustible carriers such as alumina, titania, thorium, zirconia, silica, silica-alumina, silica-magnesia, or silica-zirconia. Platinum, palladium, rhodium, and other rare metals may be employed preferably in the metallic state supported on the same non-combustible type of carriers. In operating my process on a cyclic basis, the catalyst can be regenerated at intervals by treatment with air or oxygen at temperatures above 900° F.

The preferred catalyst is chromia-alumina. Molybdena-alumina catalysts are more active than chromia-alumina but the former may produce more carbon and sulfur on the catalyst. Chromia-alumina catalysts which are generally known in the petroleum processing field can be utilized; and these catalysts usually contain from about 1.0% to about 25% or more by weight of chromia. The activity of the chromia-alumina system can be appreciably enhanced by the use of promoters which can include for instance silica, beryllium, boron, potassium and cerium. A specific catalyst found effective contains about 12% chromia, 86% alumina, and about 2% magnesium oxide as a promoter.

The products of my hydroconversion reaction are aromatic gasoline, naphthalene, beta-methylnaphthalene and other alkylnaphthalenes. These products can be separated by fractional distillation. The naphthalene and beta-methylnaphthalene are of high purity, substantially free from sulfur and nitrogen-containing impurities, and are practically completely aromatic. Beta-methylnaphthalene and the other alkylnaphthalenes can be converted to naphthalene as for instance by recycling to the second stage of my process the aromatic oil boiling above about 400° F. from which the naphthalene has been separated. 2,6-dimethylnaphthalene may be isolated by cooling, filtering and recrystallization from the dimethylnaphthalene fraction either from the first or second stage products. Also, when beta-methylnaphthalene and/or 2,6-dimethylnaphthalene as well as naphthalene are separated from the reaction product of the second stage, the remaining oil boiling above about 400° F. can be recycled to the second stage reaction.

In view of the lower concentration of naphthalene precursors in my extract fraction boiling in the range of about 400° to 460° F., I prefer the procedure in which the extract is fractionated or topped at about 460° F. before charging to the hydroconversion reaction. In this case the 400° to 460° F. cut of the product from the hydroconversion reaction will be much more concentrated in naphthalene, thus facilitating recovery and purification of naphthalene. The overhead cut obtained by topping can be suitable for use in diesel fuels, household heating fuels and catalytic cracking feed stocks and for these purposes can be blended with the raffinate from the extraction operation.

The following specific examples will serve to illustrate the present invention but they are not to be considered limiting.

Example I

7722 grams of a light cycle oil derived from the catalytic cracking of Mid-Continent gas oil in the presence of a silica-alumina catalyst and having a boiling range from about 422° to 568° F., was charged to an evacuated extraction vessel and cooled to 0° F. An amount of sulfur dioxide sufficient to give a sulfur dioxide to cycle oil ratio of 2:1 was then charged to the extraction vessel while keeping the temperature below about 10° F. The contents of the extraction vessel were cooled to -10° F. and the hydrocarbon-sulfur dioxide mixture was stirred at that temperature for five minutes. The mixture was allowed to settle for sixty minutes and the extract layer was then drawn off. Sulfur dioxide was frac-

tionated from both the extract and raffinate phases and recovered for reuse. Both the extract phase and the raffinate phase were blown with air and filtered. Pertinent data relating to this extraction procedure is as follows:

Analytical Data	Hydrocarbon Feed	Extract	Raffinate
API Gravity.....	24.2	14.3	39.3
Br. No.....	17.4	26.9	13.6
Sulfur, wt. percent.....	1.93	2.98	0.32
Mol. Wt. (Average).....	190	174	240
Spec. Dispersion.....	197.2	249.7	121.6
Aniline Point.....	29.3	<-6	76
n_D^{25}	1.5169	1.5584	1.4599

The aromatic-rich extract oil was topped at 460° F. to afford an extract composed of about 88 weight percent of aromatics. The topped extract was charged at a space velocity of .55 volume per hour per volume of catalyst to a reactor containing 270 grams of a chromia-alumina catalyst (12% Cr₂O₃ and 2% MgO). The catalyst was maintained at a temperature of about 1100° F. and a pressure of 400 p.s.i.g. and hydrogen was supplied to the reactor at the ratio of about 5.37 moles per mole of feed. The reaction continued for two hours and the following products were obtained.

Product	Weight Percent of Aromatic Oil Feed
Liquid.....	66.2
C ₄ in gas.....	2.1
Dry gas.....	24.6
Carbon on catalyst.....	7.0
Sulfur on catalyst.....	2.5
Hydrogen Sulfide.....	102.4
Total.....	

The liquid product was distilled and the following products were separated.

Product	Weight Percent of Aromatic Oil Feed
Gasoline (C ₄ to 400° F.).....	27.7
Naphthalene.....	10.1
β-Methylnaphthalene.....	12.5
Balance of naphthalenic product.....	13.4
Bottoms.....	4.6
Total.....	68.3

Example II

A light cycle oil derived by catalytic cracking of a Mid-Continent gas oil in the presence of a silica-alumina catalyst and having a boiling range of about 422° F. to 568° F. was diluted with normal heptane and contacted with activated silica gel adsorbate. After eluting with additional n-heptane, the adsorbed hydrocarbon was separated from the silica gel by means of acetone to obtain an aromatic rich extract having about 80 weight percent aromatics and 20 weight percent olefins and an API gravity of 10.7, N_D^{25} of 1.575 and a specific dispersion of 255. The aromatic extract was charged at a rate of 1.43 LHSV to a reactor containing 270 grams of a molybdena-alumina catalyst (10.4% MoO₃ and 5% SiO₂). The catalyst was maintained at a temperature of about 1025° F. and a pressure of 400 p.s.i.g. and hydrogen was supplied to the reactor on a once-through basis at a ratio of 5.79 moles per mole of feed. The

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reaction continued for one and a half hours and the following products were obtained:

Product	Weight Percent of Aromatic Oil Feed
Liquid.....	60.4
C ₄ + in gas.....	1.2
Dry gas.....	26.2
Carbon on catalyst.....	5.6
Sulfur on catalyst.....	1.1
Total.....	94.5

The liquid product was distilled and the following products were separated.

Product	Weight Percent of Aromatic Oil Feed
Gasoline (C ₄ to 400° F.).....	20.6
Naphthalene.....	14.3
1-methylnaphthalene.....	7.3
2-methylnaphthalene.....	10.6
Bottoms.....	2.5
Total.....	55.3

I claim:

1. The method of producing naphthalene which comprises extracting with a material selective for aromatics a light catalytic cycle oil derived by cracking a petroleum hydrocarbon oil in the presence of an acidic catalyst, said light cycle oil having a boiling range within about 400° to 600° F., said extracting being under conditions to produce an aromatic rich extract of n_D^{25} of about 1.55 to 1.61 and a specific dispersion of about 200 to 270, hydroconversion of the extracted oil by contacting the extracted oil in the presence of hydrogen and a hydroforming catalyst having a non-combustible base at reaction conditions of severity defined by temperature and space velocity of from about 1050° to 1150° F.

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at 0.5 LHSV and at a pressure of at least about atmospheric to form naphthalene, and separating the naphthalene from the hydroconversion product.

2. The method of claim 1 in which the extracted oil is topped to remove materials boiling below about 460° F. and the topped extract is subjected to hydroconversion.

3. The method of claim 1 in which the product of the hydroconversion boiling above about 400° F. from which the naphthalene has been recovered, is recycled to the hydroconversion.

4. The method of producing naphthalene which comprises extracting with sulfur dioxide a light catalytic cycle oil derived by cracking a petroleum hydrocarbon oil in the presence of silica-alumina catalyst, said light catalytic cycle oil having a boiling range within about 400° to 600° F., said extracting being under conditions to produce an aromatic rich extract of n_D^{25} of about 1.55 to 1.61 and a specific dispersion of about 200 to 270, hydroconversion of the extracted oil by contacting the extracted oil in the presence of hydrogen and a chromia-alumina catalyst at reaction conditions of severity defined by temperature and space velocity of about 1050° to 1150° F., at 0.5 LHSV and about 200 to 500 p.s.i.g. hydrogen partial pressure to form naphthalene, and separating the naphthalene from the hydroconversion product.

5. The method of claim 4 in which the extracted oil is topped to remove materials boiling below about 460° F. and the topped extract is subjected to the hydroconversion.

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