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## PROCESS FOR MAKING NAPHTHALENE

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This invention relates to the production of naphthalene from petroleum sources. More specifically, our invention is concerned with the production of naphthalene by an economically feasible process which includes the conversion of a selected petroleum fraction in the presence of a defined partial pressure of free hydrogen while in contact with a hydroforming catalyst under reaction conditions which are particularly selected to afford the desired result.

For years petroleum refiners have been trying to find a process for manufacturing naphthalene from petroleum which is economically feasible but to our knowledge none has yet been developed upon which a successful commercial venture has been based. In spite of the disappointments of many researchers in their prior efforts in their respect, the attractiveness of an economically feasible petroleum naphthalene process is so compelling that again and again a research program is started to attain this end. Pitfalls along the route are several; for instance, under certain severe reaction conditions which have been proposed for converting aromatic-containing cycle oils to obtain products richer in naphthalene, the other constituents of the feed are devalued to an extent which defeats the process as naphthalene yield has not been high enough to allow economic manufacture considering the degree of fuel degradation. These processes are represented by methods using the water-gas reaction and hydrolysis. In a process where yield is inadequate a larger quantity of feed must be degraded per pound of naphthalene produced. In addition the plant size and operating costs are proportionately higher on a per pound of product basis. Another limiting factor in certain processes is high coke laydown. A relatively small increase in coke laydown in terms of percent carbon on the catalyst can make the process economically infeasible due to the increased regeneration requirements which severely limit most catalytic processes for the conversion of petroleum.

In the present invention we have found an economically feasible process for producing naphthalene from petroleum sources. This process provides a balance of each of the important factors such as naphthalene yield, feed degradation and coke laydown which presents a commercially feasible process as defined by present economic conditions.

The present process can be effected in a relatively simple reaction system composed of available equipment, and it affords a high yield of naphthalene of high quality which can be easily purified to the desired extent. The success of our process is dependent upon the combination of several factors which must be met if the desired result be obtained. First, the selection of a feed stock is of the utmost significance. We have found that

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thermal tars boiling principally in the range of about 400 to about 650° F. afford an adequate yield of naphthalene and do not possess any undesirable characteristics which cannot be overcome by proper selection of processing conditions. Thermal tars which serve as our fresh feed are prepared by the catalytic cracking, for instance over a silica alumina cracking catalyst, of straight run petroleum distillates, e. g. gas oils. The cracked product, for instance predominantly as a light cycle oil, is then thermally cracked, and our feed stock is separated from the resulting products as a fraction boiling primarily in the range of about 400 to about 650° F. It is believed that both of these cracking stages serve to rearrange molecules into a form in which they can be converted to naphthalene in our process. The thermal tar feed can be obtained as an overhead, sidestream or bottoms from the distillation of the thermally cracked product; and the feed to the thermal cracking operation may contain, in addition to the catalytically cracked stocks, various components such as straight run materials, for instance reduced crude and naphtha, which may ultimately contribute to the naphthalene yield.

In addition to finding a source of a suitable feed, we have also found that the thermal tar should contain a certain minimum of naphthalenic nuclei, although we have not established that all of the naphthalene is produced from such nuclei. In fact there is considerable evidence that at least with some feeds naphthalene is produced from other structures. Regardless, of any theoretical explanation which could be proposed, we have found that the analysis of the fresh feed generally satisfies the following formula:

$$X = \text{weight percent methyl naphthalene} \times 0.7 + \text{weight percent alkyl naphthalenes of molecular weight higher than methyl naphthalene} \times 0.55 = \text{at least about } 20$$

Thus in these thermal tars when the weight percent of methyl naphthalene is multiplied by 0.7 and the value obtained then added to the weight percent of higher molecular weight alkyl naphthalenes multiplied by 0.55, the resulting figure (X) is generally at least about 20. As preferences we employ as a feed a thermal tar boiling in the range of about 400 to about 600° F. and advantageously a heart cut of the tar boiling in the range of about 430 to about 560° F. This heart cut may be separated by distillation, extraction or extractive distillation, for instance as with a solvent selective for aromatics, or any other suitable procedure or a combination of procedures.

In addition to determining that the thermal tar afforded a high yield of naphthalene, other processing conditions were found to be important. For instance, when using this feed under the conditions often proposed as optimum for producing naphthalene from refractory stocks, we found that coke laydown on the catalyst was excessive with respect to providing an economically attractive operation. As it is impractical to use a catalytic system which has to be regenerated too frequently, the coke laydown characteristics of the thermal tar under these conditions were quite disadvantageous. Thus as carbon laydown on the catalyst increases its activity declines and to maintain an acceptable activity level the regeneration to processing time ratio increases. This, of course, is an undesirable result.

We have found that to provide a sufficient diminution in coke or carbon laydown when using the thermal tar feed, a defined relationship between the partial pressures

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of free hydrogen and the hydrocarbon feed boiling above about 400° F. should be observed. The following formula expresses this relationship:

$$\frac{(\text{PH}_2)^2}{\text{PHC}} [e^{0.00435(1060 - ^\circ \text{F})}] =$$

at least about 2500 preferably at least about 3500

where

PH<sub>2</sub> is the hydrogen partial pressure, p. s. i. a.

PHC is the partial pressure in p. s. i. a. of the hydrocarbon feed boiling above about 400° F.

e is the base of the natural logarithm

° F. is the average reaction temperature in degrees Fahrenheit

These partial pressure conditions are given with reference to the beginning of our catalytic reaction or contacting zone, that is at the entrance to the initial portion of catalyst whether there be one reactor or a plurality of reactors in series. Also the PH<sub>2</sub> is at least about 400 p. s. i., preferably at least about 550 p. s. i. Thus two important features of our process are the selection of the feed stock and the hydrogen to hydrocarbon partial pressure ratio.

Our thermal tar feed can be employed successfully providing certain reaction conditions are maintained. As noted, the conversion process is conducted in the presence of free hydrogen and the partial pressure of this gas supplied to the reaction zone has been defined. Ordinarily, the hydrogen gas is provided by recycle from the reaction zone off-gases preferably after any hydrogen sulfide has been removed. Diluent gases such as methane, nitrogen, ethane, etc. can also be supplied to the reaction zone either by separate addition or by recycle. The upper limit on the amount of hydrogen which can be employed is an economical consideration and usually we do not exceed about 20 moles per mole of hydrocarbon feed boiling above about 400° F. The average conversion temperature ranges from about 950 to about 1200° F. with about 1050 to 1150 being preferred, while the reaction pressure of free hydrogen and hydrocarbon boiling above about 400° F. must be at least about 500 p. s. i. and, for instance, from about 500 to about 1200 p. s. i. with about 600 to about 800 p. s. i. being most advantageous.

The feed to the reaction zone is usually contacted with the catalyst at space velocities of about 0.5 to about 5.0 WHSV (weight of hydrocarbon feed boiling above about 400° F. per weight of catalyst per hour), and space velocities of about 0.75 to about 2.0 WHSV are preferred. Higher space velocities might be employed but would make necessary the use of greater recycle ratios. Various combinations of these reaction conditions can be employed but usually the conditions are selected to give a severity of reaction which produces an acceptable yield of naphthalene with low carbon laydown. With higher temperatures, we can employ lower pressures or higher space velocities to obtain a given severity. Higher severities afford gasoline of higher octane as the light product but increased severity decreases gasoline yield. These reaction conditions afford a good naphthalene yield—low carbon laydown balance, and the naphthalene product is light in color and low in sulfur and nitrogen, particularly when compared with crude coal tar naphthalene.

The catalysts which can be employed in the present process are non-carbon based hydroforming catalysts which can contain for example minor amounts of chromium, molybdenum, tungsten, cobalt or vanadium or mixtures of these, preferably deposited as oxides on inorganic, non-combustible carriers such as alumina, spinels, titania, thorina, zirconia, silica, silica-alumina, silica-magnesia and silica-zirconia. Platinum, palladium, rhodium and other rare metals may be employed when supported on the same non-combustible-type carriers.

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The preferred catalysts include molybdenum and alumina; cobalt, molybdenum and alumina, and particularly chromium and alumina in view of several considerations such as naphthalene yield and coke laydown. 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 of chromia. The activity of the chromia-alumina system can be enhanced by the use of promoters which can include, for instance, silica, beryllium, boron, potassium and cerium. In operating our process on a cyclic basis the catalyst can be regenerated at intervals by treatment with air or oxygen at temperatures above about 900° F. Although the catalysts have been defined as hydroforming catalysts, this is not limiting as to the nature of our reaction system. For instance, we can obtain substantial hydrodealkylation and aromatization. Also, to a lesser degree we might accomplish isomerization and certain hydrocracking reactions other than hydrodealkylation.

In the present process naphthalene can be separated from the reaction products by distillation in the cut boiling up to about 430° F. and the higher boiling ends which include methyl naphthalene and dimethyl naphthalene can be recycled to the reaction zone or withdrawn as products as desired. For instance, β-methyl naphthalene and 2,6-dimethyl naphthalene can be isolated by cooling, filtering and recrystallization of the appropriate fractions, and when desired a wider naphthalene cut can be taken. The nature of the naphthalene product is such that in most instances we can economically separate naphthalene in the 415 to 430° F. fraction.

Even though the naphthalene product is of exceptional quality, it may be desirable depending upon economics to obtain an even purer product. Naphthalene frequently contains substantial amounts of impurities which are very difficult to separate especially when the naphthalene is derived from coal tar. We have found that the naphthalene of the present invention can be purified rather easily by recrystallization from organic solvents for naphthalene. These solvents can advantageously be non-aromatic and aromatic solvents having a boiling point sufficiently below that of naphthalene so that the solvent can be separated from the naphthalene by distillation. Thus, the solvents we prefer selectively dissolve naphthalene from the impurities and contain up to about 10 carbon atoms. Apparently, this results either because of the selected feed stock we employ or the reaction conditions or both. The purification can be effected by mixing and preferably dissolving the naphthalene fraction in the solvent, cooling, filtering or otherwise separating solids and then removing the solvents from the crystals. If desired, a plurality of these solvent treatments can be effected. Suitable solvents include the normal and branch chained saturated and unsaturated aliphatic and cycloaliphatic hydrocarbons of about 4 to about 10 carbon atoms such as isobutylene, pentane, hexane, cyclohexane, diisobutylene, methylcyclopentane, heptane, and iso-octane. Other solvents which are useful and which generally contain up to about 10 carbon atoms include oxygenated solvents such as alcohols, ketone, esters and ethers; chlorinated hydrocarbons and nitriles; but of course these are more expensive than the preferred hydrocarbon solvents. Representative of the more expensive solvents are methanol, isopropanol, acetone, methyl isobutyl ketone, carbon tetrachloride, amyl acetate and acetonitrile. Mixtures of the various solvents can be employed and successive washes with different solvents also are effective. Representative solvent to naphthalene fraction ratios are about 1 to 10:1 with about 1 to 5:1 being preferred. The solvent can include extraneous materials such as components of greater molecular weight; however, if the amount of such materials becomes too great the efficiency of the purification may be decreased.

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In operating our process the catalyst can be maintained in a bed which is stationary, fluidized or moving. There is usually a net consumption of the hydrogen in the process which may be supplied from a separate source as previously noted or a hydrogen producer such as naphtha may be charged to the reactor concurrently with the feed stock to produce the needed hydrogen while being reformed.

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

#### EXAMPLE I

A chromia-alumina catalyst (12%  $\text{Cr}_2\text{O}_3$ , 2%  $\text{MgO}$ ) was charged to a reactor and brought to a temperature of about 1103° F. A thermal tar side stream of the following analysis was charged to the reactor at a space velocity of about 1.0 WHSV:

|                                |      |
|--------------------------------|------|
| X                              | 26.0 |
| Gravity API/60° F.             | 18.7 |
| Sulfur, wt. percent            | 0.13 |
| Olefins (ES45A), wt. percent   | 16.2 |
| Aromatics (ES45A), wt. percent | 50.8 |
| Bromine number                 | 14.5 |
| Boiling point—                 |      |
| Initial                        | 458  |
| 50%                            | 501  |
| End point                      | 595  |

This thermal tar was produced by cracking of coastal straight run gas oil (approximately 450–750° F. boiling range) over a fixed bed (800° F. bed outlet and 140

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of product was subjected to further distillation to give the following:

| Bolling Range of Fraction, ° F. | Component Weight Percent of Feed | Analysis of Component Weight Percent                                 |
|---------------------------------|----------------------------------|----------------------------------------------------------------------|
| 400–415                         | 1.2                              | 27.3 naphthalene, 0.1 $\beta$ -methyl naphthalene.                   |
| 415–425                         | 18.5                             | 87.1 naphthalene, 0.3 $\beta$ -methyl naphthalene.                   |
| 425–450                         | 3.0                              | 52.6 naphthalene, 32.7 $\beta$ -methyl naphthalene, 6.2 naphthalene. |
| 450–475                         | 17.7                             | 2.5 $\alpha$ -methyl naphthalene, 84.1 $\beta$ -methyl naphthalene.  |
| 475–520                         | 8.0                              | 78.0 alkyl naphthalenes (M. W. 166).                                 |
| 520–560                         | 1.9                              | 32.6 alkyl naphthalenes (M. W. 170).                                 |
| Bottoms                         | 2.3                              |                                                                      |

The ultimate naphthalene yield was 34.2 weight percent based on the feed. The  $\text{C}_5$  to 400° F. gasoline fraction had an API gravity/60° F. of 35.9, and a Reid vapor pressure of 4.95.

#### EXAMPLES II, III, IV, V, VI AND VII

Employing the manipulative procedure of Example I, several additional reactions were conducted and the specific reaction conditions employed and the results obtained are tabulated immediately below. The catalyst in Examples II, III, IV and V was that of Example I, while the catalyst of Example VI was molybdena-alumina (10%  $\text{MoO}_3$ ) and the catalyst of Example VII was cobalt-molybdena-alumina (2.5% Co, 8.5%  $\text{MoO}_3$ ).

Table I

|                                                      | Example II | Example III | Example IV | Example V | Example VI | Example VII |
|------------------------------------------------------|------------|-------------|------------|-----------|------------|-------------|
| Feed:                                                |            |             |            |           |            |             |
| Gravity API, 60° F.                                  | 17.1       | 17.1        | 17.1       | 17.1      | 21.0       | 21.0        |
| Sulfur, wt. percent                                  | 1.26       | 1.26        | 1.26       | 1.26      | 0.11       | 0.11        |
| Olefins (ES45A), wt. percent                         | 47.0       | 47.0        | 47.0       | 47.0      | 16.7       | 16.7        |
| Aromatics (ES45A), wt. percent                       | 30.0       | 30.0        | 30.0       | 30.0      | 48.8       | 48.8        |
| Bromine number                                       | 41.4       | 41.4        | 41.4       | 41.4      | 6.0        | 6.0         |
| X                                                    | 25.0       | 25.0        | 25.0       | 25.0      | 21.8       | 21.8        |
| Reaction Conditions:                                 |            |             |            |           |            |             |
| Pressure, p. s. i. g.                                | 1,000      | 700         | 700        | 700       | 700        | 710         |
| Temperature, ° F.                                    | 1,101      | 1,101       | 1,099      | 1,048     | 1,047      | 1,039       |
| Space velocity, WHSV                                 | 1.0        | 1.0         | 1.0        | 1.0       | 1.0        | 2.0         |
| H <sub>2</sub> /Feed mole ratio                      | 6.8        | 17.0        | 7.0        | 7.09      | 7.3        | 8.6         |
| $(\text{PH}_2)^2$ [e <sup>0.00435(1060-° F.)</sup> ] | 5,040      | 9,600       | 3,710      | 4,680     | 4,860      | 6,140       |
| PHC                                                  |            |             |            |           |            |             |
| Hydrogen Consumption:                                |            |             |            |           |            |             |
| Cubic feet/barrel of feed                            | 2,000      | 1,850       | 1,650      | 1,400     | 2,100      | 1,350       |
| Length of Run, hrs                                   | 2.5        | 2.5         | 2.5        | 2.5       | 2.5        | 4.5         |
| Recovery (wt. percent feed):                         |            |             |            |           |            |             |
| C <sub>5</sub> –400° F.                              | 16.0       | 16.2        | 19.4       | 17.2      | 16.2       | 22.4        |
| 400–600° F.                                          | 44.6       | 53.1        | 48.7       | 40.5      | 38.6       | 45.2        |
| 600° F. +                                            | 1.6        | 2.6         | 1.5        | 1.7       | 1.0        | 2.2         |
| Gas, total, wt. percent Feed                         | 40.9       | 30.7        | 31.3       | 25.1      | 38.3       | 31.5        |
| Catalyst:                                            |            |             |            |           |            |             |
| Carbon                                               | 1.0        | 0.4         | 1.7        | 0.7       | 1.0        | 0.9         |
| Sulfur                                               | 0.2        | 0.2         | 0.1        | 0.1       | 0.1        | 0.1         |
| Ultimate Naphthalene Yield, wt. percent feed         | 29.7       | 29.3        | 29.8       | 27.7      | 30.6       | 31.2        |

p. s. i. g.) of silica alumina catalyst and by thermal cracking (450–960° F. and 695–450 p. s. i. g. from inlet to outlet) of an approximately 400 to 700° F. boiling range fraction from the catalytically cracked product mixed with reduced crude and with heavy gas oil from the fixed bed unit. Hydrogen was supplied to the reactor at the rate of 7.0 moles per mole of hydrocarbon under a pressure of 700 p. s. i. g. The relation-

$$\frac{(\text{PH}_2)^2}{\text{PHC}} [e^{0.00435(1060-° F.)}]$$

ship was 3690. After a run of 2.5 hours, the product recovered analyzed 67.6 weight percent of feed as liquid and 34.6 weight percent of feed as gas, and the catalyst contained 0.7 weight percent of the hydrocarbon feed as carbon and 0.1 weight percent sulfur. The hydrogen consumed was 1600 ft.<sup>3</sup>/bbl. of feed. The liquid product contained 15% based on feed of hydrocarbons boiling up to about 400° F. and the 400 to 600° F. fraction

The thermal tar feed stock of Examples II to V was an initial boiling point to 600° F. fraction derived by thermal cracking (900° F. and 30 p. s. i. g.) of light cycle oil obtained by fluid cracking (910° F. and 9 p. s. i. g.) of a fraction predominantly a Mid-Continent straight run light gas oil using a silica alumina catalyst. The feed stock of Examples VI and VII was a blend of the thermal tar of Example I and bottoms from the thermal cracking operation described in Example I fractionated to about 560° F. end point.

It can be clearly illustrated that the proper selection of the feed stock is essential to the success of our process even if our reaction conditions are employed. Stated in another way, with a given crude oil source the use of our thermal tar leads to significant yield advantages over the results obtained when using catalytic cycle oils which have been frequently suggested as a feed source for naphthalene production. To illustrate this point a light cycle oil (initial to 600° F.) from the fluid catalytic

cracking of a Mid-Continent straight run gas oil was employed as a feed while employing the catalyst of Example I and the listed reaction conditions. The data pertinent to this run are:

## RUN 1

## Conditions:

|                                                   |      |
|---------------------------------------------------|------|
| Pressure, p. s. i. g.                             | 700  |
| Temp., ° F.                                       | 1105 |
| WHSV                                              | 1.0  |
| H <sub>2</sub> /feed mol. ratio                   | 8.3  |
| $\frac{(PH_2)^2}{PHC} [e^{0.00435(1060 - ° F.)}]$ | 4350 |

## Feed:

|                                |      |
|--------------------------------|------|
| Gravity API, 60° F.            | 28.2 |
| Sulfur, wt. percent            | 0.61 |
| Olefins (ES45A), wt. percent   | 25.2 |
| Aromatics (ES45A), wt. percent | 39.3 |
| X                              | 11.2 |

|                                                   |      |
|---------------------------------------------------|------|
| Hydrogen consumption, ft. <sup>3</sup> /bbl. feed | 2100 |
| Length of run, hrs.                               | 2.5  |

## Recovery, wt. percent feed:

|                         |      |
|-------------------------|------|
| C <sub>5</sub> -400° F. | 20.0 |
| 400-600° F.             | 29.8 |
| 600° F. +               | 2.7  |

|                              |      |
|------------------------------|------|
| Gas, total, wt. percent feed | 49.7 |
|------------------------------|------|

## Catalyst:

|        |     |
|--------|-----|
| Carbon | 1.6 |
| Sulfur | .0  |

|                                              |      |
|----------------------------------------------|------|
| Ultimate naphthalene yield, wt. percent feed | 20.8 |
|----------------------------------------------|------|

By comparing the data of Run 1 which employed our operating conditions but a catalytic cycle oil feed stock generally suggested as a suitable naphthalene source with the data of Example IV obtained under essentially the same reaction conditions but with our thermal tar feed of similar crude source the advantages of our process are demonstrated. In Example IV the yield of naphthalene was 29.8% while in Run 1 using the cycle oil feed the naphthalene yield was only 20.8%. Thus the results obtained in the process of our invention are dependent upon the proper selection of the feed stock.

To show that the results produced by the process of the present invention are advantageous when compared with results of processes employing the same feed stock and essentially the same reaction conditions but with an undesirably low hydrogen to hydrocarbon partial pressure relationship, a reaction was conducted with the feed and reaction conditions similar to those of Example IV except that the

$$\frac{(PH_2)^2}{PHC} [e^{0.00435(1060 - ° F.)}]$$

was 2350. The data pertinent to this run are:

## RUN 2

## Reaction conditions:

|                                                   |      |
|---------------------------------------------------|------|
| Pressure, p. s. i. g.                             | 700  |
| Temperature, ° F.                                 | 1100 |
| Space velocity, WHSV                              | 1.0  |
| H <sub>2</sub> /feed mole ratio                   | 4.74 |
| $\frac{(PH_2)^2}{PHC} [e^{0.00435(1060 - ° F.)}]$ | 2350 |

|                                                 |      |
|-------------------------------------------------|------|
| Hydrogen consumption: Cubic feet/barrel of feed | 1600 |
| Length of run, hrs.                             | 2.5  |

## Recovery, wt. percent feed:

|                         |      |
|-------------------------|------|
| C <sub>5</sub> -400° F. | 13.2 |
| 400-600° F.             | 49.7 |
| 600° F. +               | 3.0  |

|                             |      |
|-----------------------------|------|
| Gas, total wt. percent feed | 32.4 |
|-----------------------------|------|

## Catalyst:

|        |     |
|--------|-----|
| Carbon | 4.1 |
| Sulfur | 0.2 |

|                                              |      |
|----------------------------------------------|------|
| Ultimate naphthalene yield, wt. percent feed | 28.5 |
|----------------------------------------------|------|

By comparing the data of Run 2 immediately above with those obtained in Example IV the latter being conducted in accordance with the present invention, the advantages afforded by our process are apparent. For instance, note that in Example IV the naphthalene production was 29.8% and at the same time the carbon laydown was only 1.7%. Comparing these results with those of Run 2, the naphthalene production in Run 2 was favorable but was accompanied by a carbon laydown of 4.1%. The results of Run 2 are highly disadvantageous and establish along with the results of Example IV and Run 1 compared above that the success of our process is dependent upon the feed stock and reaction conditions.

Another run was made employing the thermal tar and catalyst of Examples II to V and a fairly high hydrogen to hydrocarbon molar ratio; however, the hydrogen partial pressure was below 400 p. s. i. and the

$$\frac{(PH_2)^2}{PHC} [e^{0.00435(1060 - ° F.)}]$$

was only 2120. The pertinent data were:

## RUN 3

## Reaction conditions:

|                                 |      |
|---------------------------------|------|
| Pressure, p. s. i. g.           | 400  |
| Temperature, ° F.               | 1099 |
| Space velocity, WHSV            | 0.5  |
| H <sub>2</sub> /feed mole ratio | 6.93 |

$$\frac{(PH_2)^2}{PHC} [e^{0.00435(1060 - ° F.)}]$$

|                                                 |      |
|-------------------------------------------------|------|
| Hydrogen consumption: Cubic feet/barrel of feed | 1600 |
| Length of run, hrs.                             | 2.5  |

## Recovery, wt. percent feed:

|                         |      |
|-------------------------|------|
| C <sub>5</sub> -400° F. | 14.3 |
| 400-600° F.             | 44.0 |
| 600° F. +               | 3.0  |

|                              |      |
|------------------------------|------|
| Gas, total, wt. percent feed | 32.0 |
|------------------------------|------|

## Catalyst:

|        |     |
|--------|-----|
| Carbon | 5.5 |
| Sulfur | 0.3 |

|                                              |      |
|----------------------------------------------|------|
| Ultimate naphthalene yield, wt. percent feed | 29.0 |
|----------------------------------------------|------|

These data again show an undesirably high carbon laydown on the catalyst. Also, as in Run No. 2, the C<sub>5</sub>-400° F. gasoline yield was low.

To illustrate the method of purifying the naphthalene product of this invention through recrystallization from a solvent the following specific example is included as exemplary.

## EXAMPLE VIII

The crude naphthalene fraction purified in this example was the 415-425° F. cut separated in Example I. 25.7 grams of crude naphthalene which had a freezing point of 75.2° C. obtained from a time-temperature curve and which analyzed 87.1% naphthalene by ultraviolet light adsorption spectra were dissolved in 27.3 grams of light naphtha boiling at about 152 to 160° F. The mixture was heated to 55° C. and slowly cooled to 0° C. and filtered at this temperature. The resulting crystals were dried with air while remaining on the filter. The resulting crystalline product had a freezing point of 79.4° C. obtained from a time-temperature curve and was 97.7% naphthalene by ultraviolet light adsorption spectra. Thus the naphthalene product from our invention is easily purified by recrystallization in light aliphatic hydrocarbons. Purification to the desired extent can be effected by further solvent recrystallizations.

This application is a continuation-in-part of our application Serial No. 502,531, filed April 19, 1955, now abandoned.

We claim:

1. The method of producing naphthalene which comprises contacting a thermal tar, derived by catalytic and thermal cracking of a straight run petroleum feedstock, boiling in the range of about 400 to about 650° F., and satisfying the formula

$$X = \text{weight percent methyl naphthalene} \times 0.7 + \text{weight percent alkyl naphthalenes of molecular weight higher than methyl naphthalene} \times 0.55 = \text{at least about 20}$$

with a hydroforming catalyst having a non-combustible base in the presence of free hydrogen at a temperature of about 950 to about 1200° F. and a pressure of free hydrogen and hydrocarbon boiling above about 400° F. at least about 500 p. s. i., and separating a fraction rich in naphthalene, the relationship

$$\frac{(\text{PH}_2)^2}{\text{PHC}} [e^{0.00435(1060 - ^\circ \text{F.})}]$$

being at least about 2500 where  $\text{PH}_2$  is the free hydrogen partial pressure in p. s. i. a.,  $\text{PHC}$  is the partial pressure in p. s. i. a. of the hydrocarbon feed boiling above about 400° F., said partial pressures being at the beginning of the catalyst contacting zone,  $e$  is the base of the natural logarithm and ° F. is the average reaction temperature in degrees Fahrenheit, and where  $\text{PH}_2$  is at least about 400 p. s. i.

2. The method of claim 1 in which the thermal tar boils in the range of about 430 to about 560° F.

3. The method of claim 1 in which the hydrogen partial pressure is at least about 550 p. s. i. and the expressed

$$\frac{(\text{PH}_2)^2}{\text{PHC}}$$

relationship is at least about 3500.

4. The method of claim 1 in which the catalyst is chromia-alumina.

5. The method of claim 4 in which the thermal tar boils in the range of about 430 to about 560° F.

6. The method of producing naphthalene which comprises contacting a thermal tar, derived by catalytic and thermal cracking of a straight run petroleum feedstock, boiling in the range of about 400 to about 650° F., and satisfying the formula

$$X = \text{weight percent methyl naphthalene} \times 0.7 + \text{weight percent alkyl naphthalenes of molecular weight higher than methyl naphthalene} \times 0.55 = \text{at least about 20}$$

with a hydroforming catalyst having a non-combustible base in the presence of free hydrogen at a temperature of about 950 to about 1200° F., and a pressure of free hydrogen and hydrocarbon boiling above about 400° F. at least about 500 p. s. i., separating a fraction rich in naphthalene, contacting the naphthalenic fraction with an organic solvent boiling below naphthalene, and separating purified naphthalene, the relationship

$$\frac{(\text{PH}_2)^2}{\text{PHC}} [e^{0.00435(1060 - ^\circ \text{F.})}]$$

being at least about 2500 where  $\text{PH}_2$  is the free hydrogen partial pressure in p. s. i. a.,  $\text{PHC}$  is the partial pressure in p. s. i. a. of the hydrocarbon feed boiling above about 400° F., said partial pressures being at the beginning of the catalyst contacting zone,  $e$  is the base of the natural logarithm and ° F. is the average reaction temperature in degrees Fahrenheit, and where  $\text{PH}_2$  is at least about 400 p. s. i.

7. The method of claim 6 in which the thermal tar boils in the range of about 430 to about 560° F.

8. The method of claim 6 in which the catalyst is chromia-alumina.

9. The method of claim 6 in which the hydrogen partial pressure is at least about 550 p. s. i. and the expressed

$$\frac{(\text{PH}_2)^2}{\text{PHC}}$$

relationship is at least about 3500.

10. The method of claim 6 in which the solvent is a hydrocarbon.

11. The method of claim 10 in which the solvent is a light naphtha.

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