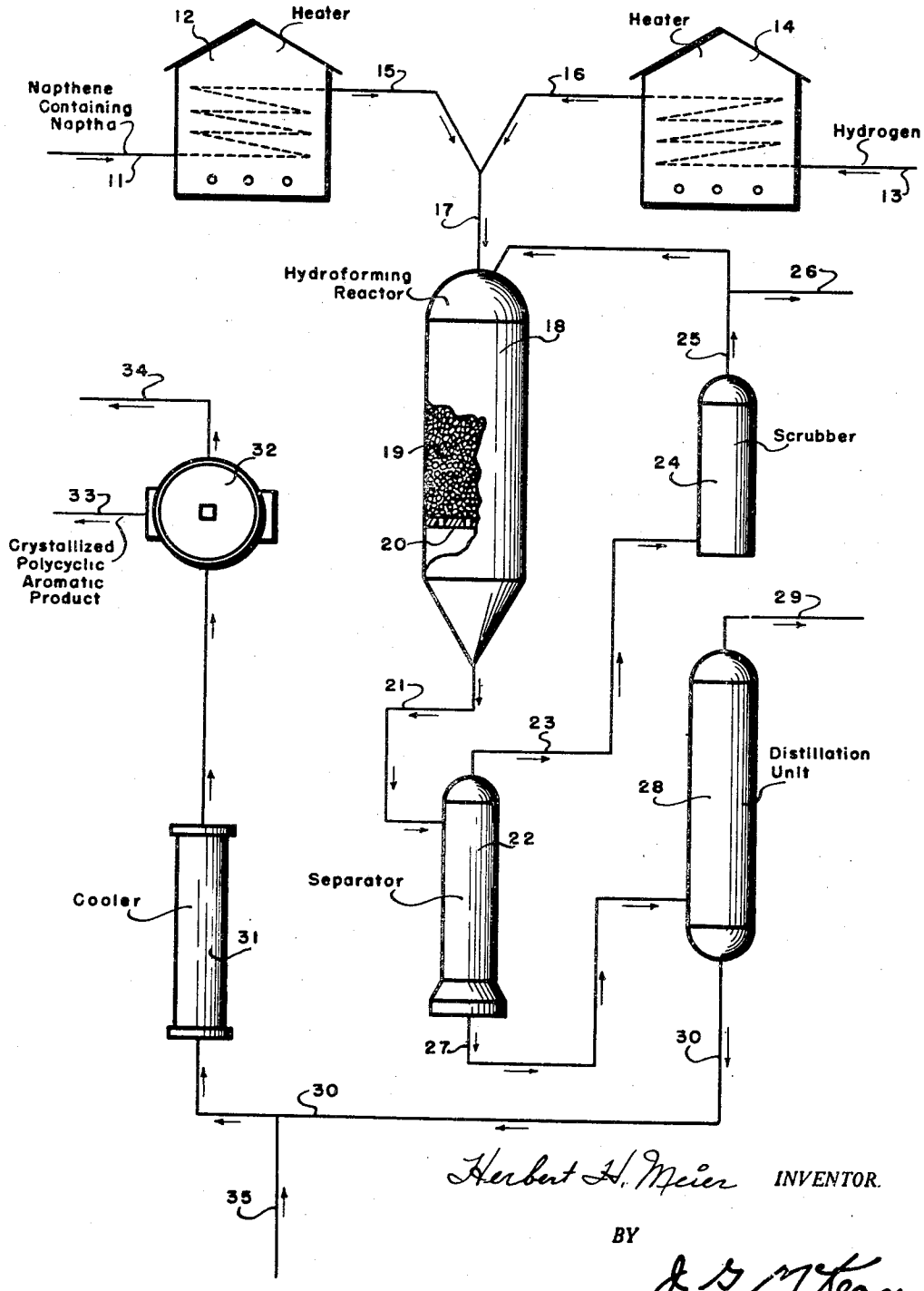
July 12, 1949. H. H. MEIER 2,475,977

PRODUCTION OF POLYCYCLIC AROMATICS

Filed Jan. 26, 1946



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Patented July 12, 1949 2,475,977

UNITED STATES PATENT OFFICE

2,475,977

PRODUCTION OF POLYCYCLIC AROMATICS

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Application January 26, 1946, Serial No. 643,797

2 Claims. (Cl. 260—668)

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The present invention is directed to a method for producing polycyclic aromatic compounds.

Polycyclic aromatic compounds are valuable materials having a variety of uses. As an example of such a compound may be mentioned naphthalene, which can be employed as the starting raw material for the production of phthalic anhydride, a chemical now much in demand. As other examples of valuable polycyclic aromatic compounds may be mentioned alpha and beta methyl naphthalenes, fluorene, diphenyl, phenanthrene, and anthracene. These polycyclic aromatic materials are obtained in limited amounts from coal tar. It is also known that limited quantities may occur in natural and cracked petroleum fractions, but the product obtained from these sources by simple distillation is contaminated with other compounds, making an expensive separation necessary if a polycyclic aromatic compound having a high degree of purity is to be obtained.

It is an object of the present invention to obtain a polycyclic aromatic compound of relatively high degree of purity from petroleum fractions. More specifically, it is an object of the present invention to process petroleum fractions comprising compounds having a polycyclic naphthenic structure to obtain relatively pure compounds having a polycyclic aromatic structure.

The present invention may be described briefly as involving the separation of a petroleum fraction including a substantial amount of material having a polycyclic naphthenic structure, the hydroforming of the fraction to convert a substantial portion of the fraction to material having a polycyclic aromatic structure, the removal of the product from the hydroforming operation and the segregation of a compound having a polycyclic aromatic structure.

As one embodiment of the present invention, a naphthenic feed stock is subjected to a distillation operation to separate a narrow boiling fraction boiling in the range of the polycyclic naphthenic derivatives of the desired polycyclic aromatic hydrocarbons. The narrow boiling fraction is hydroformed under such conditions and in the presence of such catalysts that a substantial portion of the polycyclic naphthenic hydrocarbons are converted to the polycyclic aromatic hydrocarbon having a boiling point considerably above the boiling range of the original narrow boiling fraction. The hydroformed product is then distilled to segregate a narrow boiling fraction relatively concentrated in the desired polycyclic aromatic hydrocarbon and essentially free

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of unreacted compounds contained in the charge to the hydroforming operation.

As another embodiment of the present invention a compound having a polycyclic aromatic structure and having a relatively high freezing point may be obtained in substantially purified form by preliminarily distilling a feed stock to separate a relatively narrow boiling fraction, including the desired compound having a polycyclic naphthenic structure. This narrow boiling fraction is then hydroformed. The product from the hydroforming reaction is preferably sent to a distillation step to separate a narrow boiling fraction, which includes the desired compound having a polycyclic aromatic structure. The narrow boiling fraction may then be cooled to crystallize the compound having the polycyclic aromatic structure and to liquefy at least a major portion of the other components and the crystallized compound then separated from the liquid by any of the conventional separating methods such as filtration or settling under the influence of gravity. Fractional crystallization and/or sublimation procedures well known to the art may be employed to purify further the crystalline polycyclic aromatic hydrocarbons obtained by the above-mentioned process.

Hydroforming operations have been described in literature, for example, in the Oil and Gas Journal, March 27, 1941, page 87, and in the Journal of the Institute of Petroleum, January 1944, pages 3 and 4, and may be characterized as those chemical reactions which take place when hydrocarbon oils, particularly hydrocarbons boiling in the gasoline range, are reacted at a temperature in excess of 500° F. in the presence of hydrogen and a reforming catalyst; these reactions involve a net effect of taking hydrogen away from the hydrocarbon molecules. The chemical reactions involved are complex but are generally considered to consist mainly of dehydrogenation and cyclization, although other reactions, such as cracking, hydrogenation and desulfurization, may also occur.

In the practice of the present invention it will be found convenient to separate the resultant compound having a polycyclic aromatic structure from the remainder of the product obtained from the hydroforming reaction zone by cooling the product to crystallize the compound having a polycyclic aromatic structure. The substantially pure crystallized compound having a polycyclic aromatic structure may then be separated from the remaining liquid constituents by any suitable means such as filtration or sedimentation steps.

In the practice of the present invention, it is usually desirable to distill a naphtha including a substantial portion of a compound having a polycyclic naphthenic structure to separate a relatively narrow boiling fraction, and subsequently subjecting the narrow boiling fraction to hydroforming to obtain the desired compound having a polycyclic aromatic structure. For example, if naphthalene is to be obtained as the product, it will usually be desirable to separate a fraction from a naphthenic petroleum, said fraction boiling in the range of approximately 350° to 390° F. On the other hand, to obtain anthracene and/or phenanthrene as the product it will usually be desirable to distill a naphthenic hydrocarbon to obtain a fraction boiling within the range of 500° to 600° F. and then subject the resulting fraction to hydroforming conditions.

The invention will now be described in greater detail in conjunction with the drawing, in which the sole figure is in the form of a diagrammatic flow sheet.

Referring now specifically to the drawing, a naphtha containing a substantial amount of naphthenes, for example, a Texas Coastal naphtha with at least 30 volume per cent of naphthenes, is introduced through inlet 11 and passed to a heater 12 where it is heated to a temperature within the range of 850° to 1050° F. Hydrogen or hydrogen-containing gas is discharged through inlet 13 into a furnace 14 and heated to approximately the same temperature as the naphtha in heater 12. The naphtha from heater 12 and hydrogen from heater 14 are passed through lines 15 and 16, respectively, into a line 17 where they are admixed and the mixture is discharged into a hydroforming reactor 18. In the drawing the reactor is indicated as containing a body of catalyst 19 supported on a grid 20. The mixture of naphtha and hydrogen passes downwardly through the catalyst wherein the hydroforming reaction takes place and crude product is withdrawn from the reactor chamber through outlet line 21.

As has been stated heretofore, the hydrogen in hydroforming reactor 18 results in the production of hydrogen and, accordingly, the product is passed from outlet 21 to a separator 22 where it is separated into a gaseous fraction and a liquid fraction. The mixture of gases is removed through outlet 23 and may be passed through a scrubber 24 for removing a substantial quantity of hydrocarbons and the remaining gases then recycled through line 25 to reactor 18 for further use in the process; if desired, a portion of the gas may be removed from the system through outlet 26.

The liquid portion of the product is removed from the bottom of separator 22 through outlet 27 and may be passed to a distillation unit represented in the drawing by a column 28. In the distillation unit a low boiling fraction is removed as overhead through outlet 29 and the heavier material including the desired product having a polycyclic aromatic structure is removed through outlet 30. It will be found convenient to remove the polycyclic aromatic constituent from the mixture in line 30 by solidifying the polycyclic aromatic; this may conveniently be done by passing the mixture through cooler 31 to crystallize the polycyclic aromatic material and the cooled product is then sent to a conventional device for separating solids from liquid, such as a centrifuge 32 and the solidified polycyclic aromatic removed through outlet 33 and the separated liquid removed through outlet 34. The crystallization of the polycyclic aromatic material is facilitated by the addition of several volumes of a light hydrocarbon such as isopentane to the bottoms fraction from distillation unit 28 prior to the cooling operation. The light hydrocarbon is conveniently added through line 35.

In order to illustrate further the practice of the present invention, the following examples are given.

Example I

One volume of the 360° to 390° F. fraction of a Coastal crude, which contained no naphthalene and had a specific gravity of 0.8227, was passed over an equal volume of catalyst composed of nine weight per cent molybdenum trioxide and 91 weight per cent alumina at a charge rate of one volume of liquid hydrocarbon per volume of catalyst per hour, a pressure of 200 pounds per square inch gage, a temperature of 950° F., and in the presence of added hydrogen. The hydrogen charge rate to the catalyst zone was equivalent to 2100 cubic feet of hydrogen, measured at atmospheric pressure and temperature, per barrel of liquid hydrocarbon charged. The yield of liquid product obtained from the catalyst zone was 82 weight per cent of the original hydrocarbon charged; the remainder of the hydrocarbon charge was converted to gaseous hydrocarbons, hydrogen, and a carbonaceous material that deposited on the catalyst. The hydroformed liquid product was found to contain 3.4 weight per cent naphthalene. One volume of the hydroformed liquid product was diluted with three volumes of isopentane, chilled to a temperature of −40° F., and filtered to recover white, flaky naphthalene crystals. The total yield of naphthalene recovered was 68 weight per cent of that present in the product.

Example II

1.6 volumes of the 353° to 394° F. fraction of a Coastal crude, which contained no naphthalene and had a specific gravity of 0.8227, was passed over one volume of catalyst composed of 10 weight per cent molybdenum trioxide and 90 weight per cent of zinc spinel ($ZnAl_2O_4$) at a charge rate of one volume of liquid hydrocarbon per volume of catalyst per hour, atmospheric pressure, a temperature of 1000° F., and in the presence of added hydrogen. The hydrogen charge rate to the catalyst zone was equivalent to 1780 cubic feet of hydrogen, measured at atmospheric pressure and temperature, per barrel of liquid hydrocarbon charged. The yield of liquid product obtained from the catalyst zone was 85 weight per cent of the original hydrocarbon charged; the remainder of the hydrocarbon charge was converted to gaseous hydrocarbons, hydrogen, and a carbonaceous material that deposited on the catalyst. The hydroformed liquid product was then fractionated to segregate the 66 to 92 volume per cent fraction having a boiling range of 385° to 440° F. and containing 3.1 weight per cent naphthalene. One volume of the 385° to 440° F. fraction was diluted with three volumes of isopentane, chilled to a temperature of −40° F. and filtered to recover white, flaky naphthalene crystals having a melting point of 170° F. (uncorrected for thermometer stem). The yield of naphthalene crystals recovered from the aforementioned fraction was 85 weight per cent.

Example III

1.1 volumes of the 360° to 385° F. fraction of a Coastal crude, which contained no naphthalene

and had a specific gravity of 0.8206, was passed over one volume of catalyst composed of 40 weight per cent nickel monosulfide and 60 weight per cent tungsten trisulfide at a charge rate of 0.7 volume of liquid hydrocarbon per volume of catalyst per hour, a pressure of 200 pounds per square inch gage, a temperature of 900° F., and in the presence of added hydrogen. The hydrogen charge rate to the catalyst zone was equivalent to 2940 cubic feet of hydrogen, measured at atmospheric pressure and temperature, per barrel of liquid hydrocarbon charged. The yield of liquid product obtained from the catalyst zone was 80 weight per cent of the original hydrocarbon charged; the remainder of the hydrocarbon charge was converted to gaseous hydrocarbons, hydrogen, and a carbonaceous material that deposited on the catalyst. The hydroformed liquid product was found to contain 6.0 weight per cent naphthalene. One volume of the hydroformed liquid product was diluted with three volumes of isopentane, chilled to a temperature of −40° F., and filtered to recover 87 weight per cent of the naphthalene produced in the hydroforming operation.

Example IV

2.0 volumes of the 360° to 385° F. fraction of a Coastal crude, which contained no naphthalene and had a specific gravity of 0.8206, was passed over one volume of catalyst composed of 10 weight per cent molybdenum trioxide and 90 weight per cent zinc spinel ($ZnAl_2O_4$) at a charge rate of 0.5 volume of liquid hydrocarbon per volume of catalyst per hour, a pressure of 200 pounds per square inch gage, a temperature of 922° F., and in the presence of added hydrogen. The charge rate of gas containing 62 mole per cent hydrogen to the catalyst zone was equivalent to 2460 cubic feet, measured at atmospheric pressure and temperature, per barrel of liquid hydrocarbon charged. The yield of liquid product obtained from the catalyst zone was 82.3 weight per cent of the original hydrocarbon charged; the remainder of the hydrocarbon charge was converted to gaseous hydrocarbons, hydrogen, and a carbonaceous material that deposited on the catalyst. The total liquid product was found to contain 3.9 weight per cent naphthalene. The hydroformed liquid product was then fractionated to segregate the fraction boiling above a temperature of 400° F. and representing the 81.9 to 100 weight per cent fraction of the total hydroformed product. This fraction was found to contain 23.4 weight per cent naphthalene and 5.6 weight per cent of alpha and beta methylnaphthalenes. This represents a recovery by distillation of 90.4 weight per cent of the total naphthalene produced in the hydroforming operation.

Example V

2.0 volumes of the 360° to 385° F. fraction of a Coastal crude, which contained no naphthalene and had a specific gravity of 0.8206, was passed over one volume of catalyst composed of 10 weight per cent molybdenum trioxide and 90 weight per cent zinc spinel ($ZnAl_2O_4$) at a charge rate of 0.5 volume of liquid hydrocarbon per volume of catalyst per hour, a pressure of 200 pounds per square inch gage, a temperature of 924° F., and in the presence of added hydrogen. The charge rate of gas, containing 63 mole per cent hydrogen, to the catalyst zone was equivalent to 2580 cubic feet, measured at atmospheric pressure and temperature, per barrel of liquid hydrocarbon charged. The yield of liquid product obtained from the catalyst zone was 84.0 weight per cent of the original hydrocarbon charged; the remainder of the hydrocarbon charge was converted to gaseous hydrocarbons, hydrogen, and a carbonaceous material that deposited on the catalyst. The total liquid product was found to contain 4.3 weight per cent naphthalene. The hydroformed liquid product was then fractionally distilled to segregate the fraction boiling from 420° to 530° F. and representing the 92.7 to 94.9 weight per cent fraction of the total hydroformed product. This fraction was found to contain 47 weight per cent naphthalene. This represents a recovery by distillation of 43 weight per cent of the total naphthalene produced in the hydroforming operation.

Example VI

The 300° to 540° F. fraction of a Coastal crude was solvent extracted with liquid sulfur dioxide at sub-atmospheric temperature in order to remove aromatic hydrocarbons. The aromatic-free raffinate was then fractionally distilled to segregate from it the fraction having a specific gravity of 0.7864 and boiling from 353° to 445° F. and 0.82 volume of this fraction was passed over one volume of catalyst composed of nine weight per cent molybdenum trioxide and 91 weight per cent alumina at a charge rate of one volume of liquid hydrocarbon per volume of catalyst per hour, a pressure of 200 pounds per square inch gage, a temperature of 960° F., and in the presence of added hydrogen. The hydrogen charge rate to the catalyst zone was equivalent to 2400 cubic feet of hydrogen, measured at atmospheric pressure and temperature, per barrel of liquid hydrocarbon charged. The yield of liquid product obtained from the catalyst zone was 50 weight per cent of the original hydrocarbon charged; the remainder of the hydrocarbon charge was converted to gaseous hydrocarbons, hydrogen, and a carbonaceous material that deposited on the catalyst. The hydro-formed liquid product was found to contain 10.3 weight per cent naphthalene, 8.6 weight per cent alpha methyl naphthalene, and 5.6 weight per cent beta methyl naphthalene.

Example VII

0.83 volume of the 532° to 662° F. fraction of a Coastal crude, which contained no anthracene or phenanthrene and had a specific gravity of 0.875, was passed over one volume of catalyst composed of 9 weight per cent molybdenum trioxide and 91 weight per cent of alumina at a charge rate of one volume of liquid hydrocarbon per volume of catalyst per hour, a pressure of 200 pounds per square inch gage, a temperature of 960° F., and in the presence of added hydrogen. The hydrogen charge rate to the catalyst zone was equivalent to 2400 cubic feet of hydrogen measured at atmospheric pressure and temperature per barrel of liquid hydrocarbon charged. The yield of liquid product obtained from the catalyst zone was 65 weight per cent. The remainder of the hydrocarbon charge was converted to gaseous hydrocarbons, hydrogen, and a carbonaceous material that deposited on the catalyst. The liquid product was found to contain anthracene and phenanthrene.

While I have given specific examples illustrating the practice of the present invention, it is to be understood that these examples are given by way of illustration only and are not intended to limit the scope of the invention.

The preferred catalysts to be employed in the practice of my invention are those which promote the production of high yields of polycyclic aromatic hydrocarbons without causing excessive quantities of gaseous hydrocarbons and carbonaceous materials to be formed. Such catalysts as the oxides of chromium, molybdenum, or vanadium supported on alumina or zinc spinel and those composed of the sulfides of such metals as nickel and tungsten are usually preferred although other hydroforming catalysts may be employed.

Catalyst temperatures employed during the hydroforming operation will vary depending on the stock to be hydroformed and the type of catalyst used. Naphthalene, for example, may be produced over a catalyst composed of the sulfides of nickel and tungsten at a temperature of from 850° to 950° F. In the production of the high molecular weight polycyclic aromatics such as anthracene, it is usually preferable to employ more severe temperatures in the range of 950° to 1050° F. and an active catalyst such as molybdenum trioxide supported on a suitable carrier.

The amount of hydrogen charged to the reaction zone will preferably be in the range from 500 to 4000 cubic feet per barrel of liquid hydrocarbon charged although lower or higher hydrogen charge rates than those mentioned above may be employed.

Reaction pressures will vary from atmospheric to 500 pounds per square inch gage or higher; however, it is usually desirable to employ superatmospheric pressures in the reaction zone in order to minimize the formation of undesirable side products such as gaseous hydrocarbons and carbon.

The naphtha fraction selected for the hydroforming operation is usually derived from a highly naphthenic crude such as those produced in the Coastal regions. The narrow boiling fraction to be hydroformed preferably boils in the range of the polycyclic naphthenic derivatives of the desired polycyclic aromatic hydrocarbon. The naphthenic derivatives of naphthalene, cis and trans decaline, boil respectively at 382° and 366° F. whereas naphthalene boils at 425° F. By the selection of a carefully fractionated naphtha preferably boiling in the range 360° to 385° F. for the hydroforming operation, the polycyclic naphthenes will be hydroformed to the desired aromatic with an appreciable shift in boiling range. Consequently, a simple distillation of the hydroformate will concentrate the desired polycyclic aromatic hydrocarbon or hydrocarbons as a bottoms fraction.

If it is desired to produce alpha and beta methyl naphthalene, boiling respectively at 473° and 466° F., the desired boiling range of the naphthenic fraction is about 410° to 445° F. Anthracene and/or phenanthrene having boiling points respectively of 648° and 644° F. may be produced from naphthenic fractions having a boiling range of 500° to 600° F. or if desired from narrower boiling fractions than the afore-mentioned fraction providing the fraction boils within the limits mentioned above. My invention is not limited to the production of the above-mentioned polycyclic aromatic hydrocarbons, but may be employed for the production of a wide variety of polycyclic aromatic hydrocarbons.

Having fully described and illustrated the practice of the present invention, what I desire to claim as new and useful and to secure by Letters Patent is:

1. In the production of naphthalene, the steps of segregating a petroleum naphtha feed stock which boils within the range of approximately 350° to 390° F. and which contains appreciable amounts of the naphthenic derivatives of naphthalene, contacting said naphtha with a hydroforming catalyst in a reaction zone at a temperature above 850° F. and at a pressure in the range from 0 to 500 pounds per square inch gauge in the presence of added hydrogen and under such conditions that there is an overall net production of hydrogen, converting a substantial portion of the naphthenic derivatives of naphthalene to naphthalene, withdrawing product from contact with said catalyst and distilling the product to separate a narrow boiling fraction boiling above 400° F. which comprises a substantial amount of naphthalene.

2. In the production of naphthalene, the steps of segregating a naphtha feed stock boiling from about 350° to 390° F. from a naphthenic-type crude, said naphtha containing appreciable amounts of the naphthenic derivatives of naphthalene, contacting said naphtha with a hydroforming catalyst in a reaction zone at a temperature in the range from 850° to 1050° F. and a pressure in the range from 0 to 500 pounds per square inch gauge in the presence of added hydrogen and under such conditions that there is an overall net production of hydrogen, converting a substantial portion of the naphthenic derivatives of naphthalene to naphthalene, withdrawing product from the reaction zone, distilling the product to separate a narrow boiling fraction boiling above 400° F. which comprises a substantial amount of naphthalene, cooling the narrow boiling fraction to crystallize naphthalene and to liquify at least a substantial portion of the remainder of the fraction and separating crystallized naphthalene from the remainder of the fraction.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,242,188	Heyl	Oct. 9, 1917
2,207,552	Putt	July 9, 1940
2,216,131	Pier et al.	Oct. 1, 1940
2,232,909	Gohr	Feb. 25, 1941
2,364,453	Layng et al.	Dec. 5, 1944

FOREIGN PATENTS

Number	Country	Date
49,191	France	Nov. 28, 1938
406,808	Great Britain	Mar. 8, 1934

OTHER REFERENCES

Linstead et al., Chemical Society Journal, 1937, 241 Dehydrogenation, pages 1146–1152.

Chemical Technology of Petroleum, Gruse and Stevens, 2nd edition, pages 42–44 (1942).