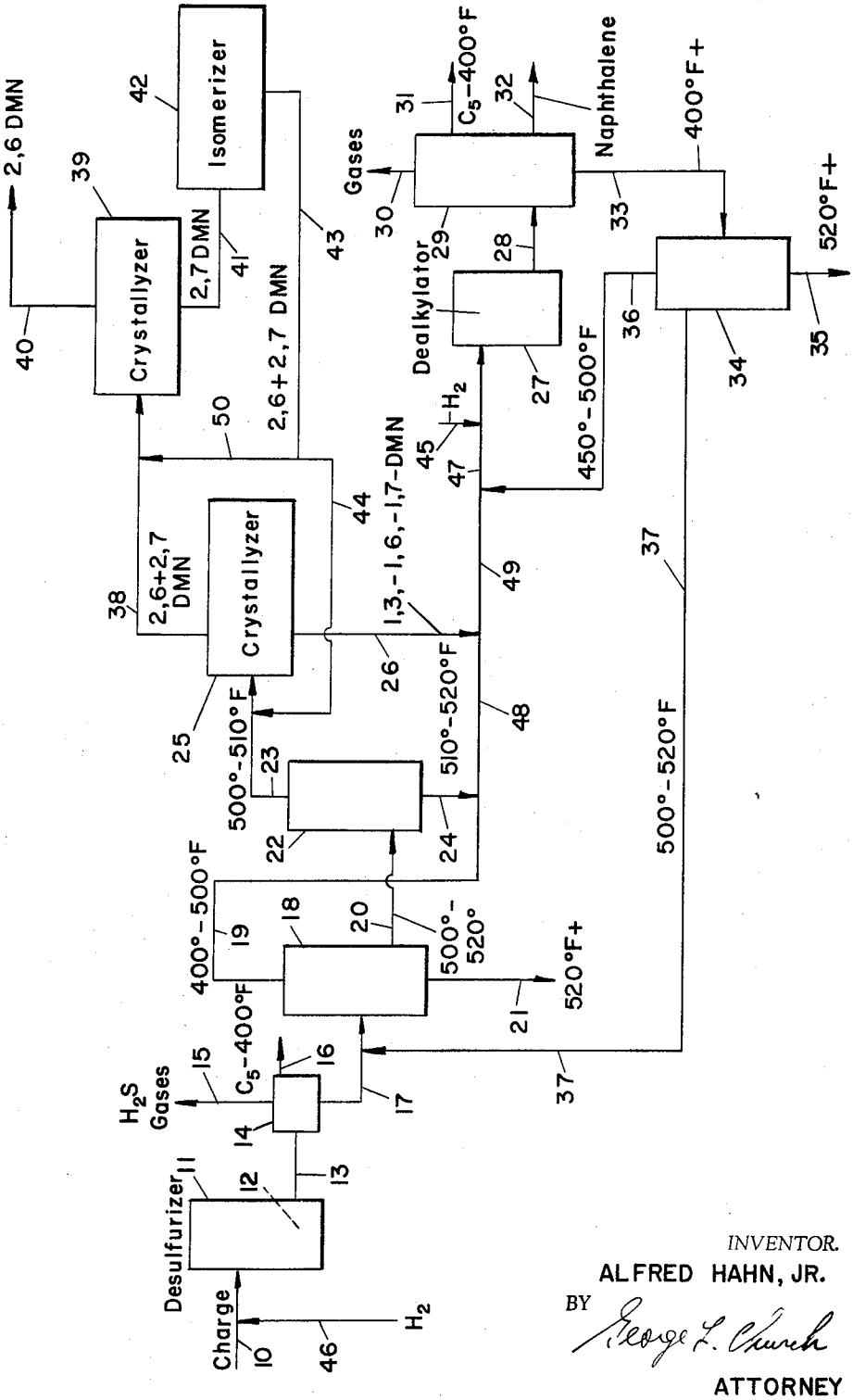
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PROCESS FOR THE PRODUCTION OF 2,6-DIMETHYLNAPHTHALENE

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PROCESS FOR THE PRODUCTION OF 2,6-DIMETHYLNAPHTHALENE

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This invention relates to the preparation of condensed-ring dicyclic aromatic hydrocarbons from charge stocks derived from petroleum gas oil. Specifically it relates to an improved process for the simultaneous production of naphthalene and 2,6-dimethylnaphthalene.

Petroleum fractions which boil within the range of 400°–500° F. generally contain substantial amounts of alkylnaphthalenes such as mono-, di-, and trimethylnaphthalenes, and in smaller quantity the ethylnaphthalenes. Recycle fractions which are formed in the cracking of petroleum stocks and which include this boiling range often include major proportions or aromatic hydrocarbons that are mainly alkylnaphthalenes. Such fractions typically have aromatic contents varying within the range of 25%–97%, but usually contain between 50% and 95%, depending upon the particular operation in which the petroleum fractions are produced. These hydrocarbon charge stocks are obtained in both catalytic and thermal cracking processes and in operations in which combinations of catalytic and thermal cracking steps are utilized. Additionally, these hydrocarbon charge stocks can be obtained as the reformate fraction from typical reforming processes, such as those using the well-known platinum catalyst. Stocks having high alkylnaphthalene contents can also be obtained by extracting straight-run petroleum fractions of appropriate boiling ranges, such as kerosene, or by extracting the above-mentioned cracked fractions, such as catalytic gas oil, with suitable solvents, for example, furfural or sulfur dioxide, or by selective adsorption using solid adsorbents, such as silica gel, activated carbon, molecular sieves, and the like. These aromatic concentrates may be composed of 100% aromatic hydrocarbons.

The present invention is directed to the production of naphthalene and 2,6-dimethylnaphthalene from petroleum hydrocarbon charge stocks of the type referred to above. Basically the charge stock used in practicing this invention is a petroleum hydrocarbon fraction boiling substantially within the range of 400°–900° F. and having an API gravity ranging from 5°–40°. Preferably the charge stock will boil between 450° and 550° F. and will be composed by weight of 35%–100% aromatic hydrocarbons including substituted condensed-ring aromatics, such as alkylnaphthalenes and from 65%–0% non-aromatic type hydrocarbons. As used throughout this disclosure, alkyl and dialkyl are understood to be those radicals each having at least one and no more than 6 carbon atoms, branched or unbranched, joined or conjoined. Also the alkyl radicals or groups will usually appear at the α and β positions on the naphthalene nucleus. This type of charge material also contains substantial amounts of sulfur components that normally occur within this boiling range. Charge stocks most typically employed have an aromatic content within the range of 50%–95% by weight and a sulfur content ranging from 1%–3%. In general, the substituted condensed-ring aromatic hydrocarbons constitute from 20%–80% of the total aromatic type hydrocarbons present in the charge stock.

It has been proposed heretofore to prepare naphthalene by subjecting aromatic hydrocarbon stocks containing alkylnaphthalenes to high temperature dealkylation in

the presence of hydrogen. As a general rule, the dealkylation conditions employed can effect only a partial dealkylation in one pass of the alkylnaphthalenes through the reactor. In order to increase the yield of naphthalene, it is desirable to fractionate the reaction product to obtain the desired naphthalene product, to recover another fraction comprising unconverted and only partially converted alkylnaphthalenes which is commonly recycled to the dealkylator to effect further conversion into naphthalene.

In the high temperature dealkylation processes of the kind referred to above, it is characteristic that alkyl groups in the α position are removed from the naphthalene nucleus at about twice the rate as those alkyl groups in the β position. Hence the recycle fraction obtained from the reaction product contains considerably more β-alkylnaphthalene than α-alkylnaphthalene. A typical composition of the recycle fraction is as follows:

	Percent
β-methylnaphthalene	70
α-methylnaphthalene	15
Dimethylnaphthalene	15

Based on the rates of demethylation of α- and β-methylnaphthalenes, the dimethyl portion of the recycled stream will contain 50%–70% by weight of a mixture comprising 2,6- and 2,7-dimethylnaphthalenes. According to the present invention this material is utilized in a way to produce additional amounts of naphthalene and high purity 2,6-dimethylnaphthalene as an additional product. The naphthalene is useful as the feed stock to processes which make phthalic anhydride or is useful alone as an insecticide. The 2,6-dimethylnaphthalene is extremely usful as an intermediate for the production of synthetic resins.

The invention is described more specifically with reference to the accompanying drawing which is a schematic flow sheet illustrating a combination but integrated process for producing naphthalene and 2,6-dimethylnaphthalene from petroleum charge stocks containing alkylnaphthalenes.

Referring now to the drawing, the charge material which enters the system through line **10** is a catalytic gas oil fraction boiling in the range of 440°–525° F. and containing alkylnaphthalenes. Preferably, the feed stock is a catalytic gas oil aromatic extract containing a major proportion of dicyclic aromatics together with a minor proportion of aromatics having only one aromatic ring and only a small amount of saturated hydrocarbons. For example, a preferred charge stock may contain 60% dicyclic aromatics, 35% monocyclic aromatics and 5% saturates.

The heated charge material together with hydrogen from line **46** passes through line **10** to a catalytic desulfurizer **11** which contains a desulfurization catalyst **12** such as cobalt molybdenum on alumina or molybdenum disulfide on alumina. The conditions for conducting this catalytic desulfurization and conditioning step include a temperature within the range of 800°–980° F.; pressure of 150–1000 p.s.i.g. with a range of 200–500 p.s.i.g. preferred; a hydrogen to hydrocarbon mole ratio of 3:1 to 25:1, preferably 5:1 to 15:1 and a liquid hourly space velocity of 0.5–10 (volumes of charge per hour per bulk volume of catalyst). The hydrogen consumption under these conditions should be between 65 and 500 s.c.f. per barrel of liquid feed per percent sulfur in the feed, and preferably between 200 and 400 s.c.f. per barrel. This conditioning step also effects cracking of most of the saturates and some of the monocyclic aromatic hydrocarbons. The sulfur, of course, is converted mainly into hydrogen sulfide.

From desulfurizer **11** the reaction product is sent through line **13** to fractionator **14** from which normally gaseous components are removed overhead through line **15** and a C_5 to 400° F. gasoline fraction is removed via line **16**. The 400° F. + fraction which contains primarily alkylnaphthalenes is removed through line **17**.

Referring now to the high temperature dealkylation step, material obtained as hereafter specified and composed mainly of monomethyl and dimethylnaphthalenes and a small amount of ethylnaphthalenes passes through line **47** together with hydrogen introduced via line **45** into dealkylator **27**. In the preferred embodiment of the invention the dealkylation reaction is effected thermally; that is, in the absence of any catalytic material. The conditions for this thermal dealkylation include a pressure of 150–1000 p.s.i.g., preferably 200–500 p.s.i.g.; a hydrogen to hydrocarbon mole ratio within the range of 3:1 to 25:1, preferably 5:1 to 15:1; a residence time of 2–300 seconds with a preferred residence time of 10–60 seconds; and a temperature above 1000° F., preferably within the range of 1200°–1400° F., sufficient to effect dealkylation of alkylnaphthalenes. In this reaction only a partial dealkylation occurs since the alkyl groups which are in the α position on the naphthalene nucleus are removed at about twice the rate as those in the β position. Hence the reaction product which leaves dealkylator **27** through line **28** contains, in addition to the desired naphthalene, unreacted methylnaphthalenes and partially dealkylated naphthalenes. This mixture is enriched with respect to the β-alkyl groups as compared to the charge material fed to dealkylator **27**.

In another embodiment of the invention, the dealkylation reaction which is effected in dealkylator **27** can be carried out catalytically utilizing a desulfurizing catalyst, such as cobalt molybdate or molybdenum disulfide on alumina. Frequently the presence of catalyst in this step facilitates the dealkylation reaction, and in some cases permits it to be carried out at a lower temperature than that required for thermal dealkylation. The catalyst also effects the conversion of any remaining sulfur into hydrogen sulfide and hence permits the preparation of naphthalene and 2,6-dimethylnaphthalene having a negligible sulfur content. The conditions for the catalytic dealkylation reaction include a pressure of 150–1000 p.s.i.g. with a range of 200–500 p.s.i.g. preferred; a hydrogen to hydrocarbon mole ratio of 5:1 to 25:1; a liquid hourly space velocity of 0.2–5.0; and a temperature above 1000° F., usually between 1100° F. and 1200° F., sufficient to dealkylate the alkylnaphthalene hydrocarbons and convert any remaining sulfur mainly into hydrogen sulfide.

The reaction product from line **28** passes to fractionator **29** from which gases and a C_5–500° F. aromatic gasoline fraction are removed, respectively, from lines **30** and **31**. Napthalene, as one desired product, is taken from line **32** as material boiling in the 400°–450° F. boiling range. Typically, this fraction is composed predominantly of naphthalene and has a melting point of at least 78.6° C. and a sulfur content that is less than 10 parts per million.

The 450° F. + material withdrawn from fractionator **29** via line **33** is composed mainly of monomethyl and dimethylnaphthalenes with the alkyl groups in the β position predominating. This stream also contains a small amount of material boiling above the dimethylnaphthalenes which desirably should be removed. This material is passed through line **33** to fractionator **34** from which a monoalkylnaphthalene, such as monomethylnaphthalene, concentrate boiling in the range of 450°–500° F. is obtained overhead through line **36** and passed as hereinafter shown into dealkylator **27**, a dialkylnaphthalene, such as dimethylnaphthalene, concentrate boiling from 500°–520° F. is removed through line **37**, and the higher boiling material is removed as bottoms via line **35**.

The 500°–520° F. fraction removed from fractionator **34** via line **37** is admixed with the alkylnaphthalene containing material from line **17** and passed into a fractionation section indicated by columns **18** and **22**. In column **18** material distilling below 500° F. and composed mainly of methylnaphthalenes and a small amount of ethylnaphthalenes is removed overhead and passes through line **19** with other materials hereafter specified to the dealkylator **27**. Material boiling above 520° F. is rejected from the bottom of tower **18** via line **21**, and an intermediate fraction boiling from 500°–520° F. and composed of dimethylnaphthalenes and generally a small amount of ethylnaphthalenes is taken through line **20** to tower **22**.

In tower **22** the operating conditions are adjusted to remove overhead in line **23** a 500°–510° F. cut and removes as a bottoms product a 510°–520° F. boiling range fraction. It has been found that with sufficiently good fractionation substantially all of 2,6- and 2,7-dimethylnaphthalenes that were present in the charge fraction will appear in the 500°–510° F. overhead cut. A bottom fraction which is composed of other dimethylnaphthalenes (mainly the 1,3-, 1,6- and 2,3-isomers) passes through lines **24** and **48** in admixture with the 400°–500° F. fraction in line **19** from tower **18** and other materials hereafter specified to dealkylator **27**.

The 500°–510° F. cut from line **23** will contain, in addition to substantially all of the 2,6- and 2,7-isomers, minor amounts of the 1,3-, and1,6- and 1,7-isomers, and generally a small amount of ethylnaphthalene. These other components all have freezing points considerably lower than the 2,6- and 2,7-isomers hence; this cut is passed from line **23** into a first crystallization zone containing crystallizer **25** and a separation is made by fractional crystallization. The 2,6- and 2,7-dimethylnaphthalene concentrate is removed from crystallizer **25** via line **38**. The filtrate from crystallizer **25** containing the other isomers, such as 1,3-, 1,6- and 1,7-dimethylnaphthalenes is passed through line **26** and line **49** in admixture with the material from lines **19**, **24**, and **36** through line **47** together with hydrogen from line **45** into dealkylator **27**.

The concentrate of 2,6- and 2,7-dimethylnaphthalene from line **38** is passed into a second crystallization zone containing crystallizer **39** wherein the 2,6-isomer is separated from the 2,7-isomer by fractional crystallization. Pure 2,6-dimethylnaphthalene is recovered in high yield through line **40**. The 2,7-dimethylnaphthalene isomer is removed from crystallizer **39** via line **41**.

The crystallization which takes place in crystallizer **39** to separate the 2,6-isomer from the 2,7-isomer is performed, for example, by cooling a solution of the isomer concentrate from line **38** to a temperature in the range from −30° to −60° C. though higher temperatures can be used, e.g., up to 0° C. Normally the feed material from line **38** is dissolved in a solvent at room temperature, though higher temperatures can be employed, if desired, in order to reduce the amount of solvent needed. The solvent ratio is critical but will usually be in the range from 0.5–2.5 parts by volume of solvent per part of hydrocarbon charge. Suitable solvents include the lower alcohols which are preferred. Aliphatic hydrocarbons can be employed but relatively low temperatures should be used if aliphatic hydrocarbons are employed. Mixtures of aliphatic hydrocarbons in lower alcohols may also be employed. As a rule, a suitable solvent should be able to dissolve at least one gram of hydrocarbon per 10 millimeters of solvent at 25° C. and must remain liquid at the crystallization temperatures. Suitable aliphatic hydrocarbons include propane, isobutane, n-pentane, n-hexane, heptanes, etc. Suitable alcohols include methanol, ethanol, isopropanol, n-butanol, amyl alcohols, etc. The amount of alcohol in the solvent is preferably in the range from 0–75 volume percent, preferably not more than 60 volume percent. The aliphatic hydrocarbon preferably has 3–6 carbon atoms; the alcohol, 1–4 carbon atoms. It is also contemplated that ketones, such as acetone,

methyl isobutyl ketone, etc., and the like can be substituted for, or used in conjunction with the alcohols. The solvents used can be the same in the earlier and hereinafter specified later crystallizations. The solvents used for washing filter cakes can be the same as, or different from, the solvents used in the crystallization. Preferably, they are the same.

The concentrate of 2,6-dimethylnaphthalene which has crystallized from the cooled solution is filtered or otherwise separated from the solution containing dissolved constituents of the original hydrocarbon fraction. Desirably, the filter cake is washed with solvents to remove adhering mother liquor, though this is not necessary.

The filter cake of 2,6-dimethylnaphthalene is next heated in order to melt a portion thereof. The heating is to a temperature from 5°–50° C., more preferably from 20°–30° C. The melted hydrocarbons are then removed from the unmelted portion of the filter cake, which portion constitutes a 2,6-dimethylnaphthalene in high concentration. Typically, this concentrate has a melting point in the range from 50°–75° C. However, it is still quite impure as may be seen from comparison with the melting point of pure 2,6-dimethylnaphthalene. Advantageously the heating step and the subsequent removal of melted material from the remaining solids are performed on the same filter, or in the same centrifuge, etc., that is used to separate crystals from mother liquor after the first crystallization. However, if desired, these steps can be performed in separate heating and separation zones.

The amount of crystals which is melted is preferably in the range from 5%–50% by weight of the total crystals. Lesser amounts usually do not provide optimum purification of the 2,6-dimethylnaphthalene, while greater amounts usually result in an undesirable extent of melting of 2,6-dimethyl-naphthalene. However, in general, any substantial extent of fractional melting will result in a desirable purification of the unmelted 2,6-dimethylnaphthalene.

The 2,6-dimethylnaphthalene concentrate obtained by removing melted material from the heating step is next recrystallized at a temperature ranging from −30° C. to −60° C. in the presence of a solvent.

The precipitated 2,6-dimethylnaphthalene is now removed by filtration. The filter cake can be washed using cooled solvent, but this is not essential. Following the filtration at reduced temperature, the filtered crystals are usually permitted to warm to room temperature. There may be a small amount of material in the crystals which melts during this warming, and this material may be removed by suction through the filter, aided by washing with cooled solvent, such as methanol, if desired, but such removal is not essential.

Therefore, the pure 2,6-dimethylnaphthalene which is in line **40** can be obtained by the following summary of processing steps:

(1) The material in line **38** is dissolved, in say, n-pentane.

(2) The filter cake is heated to melt a portion thereof, and the melted portion is separated from the unmelted portion by filtration.

(3) The solution is cooled and filtered.

(4) The filter cake is washed with, say, methanol, then recycled and dissolved in, say, n-pentane.

(5) The solution is cooled.

(6) The purified 2,6-dimethylnaphthalene is filtered from the pentane solution.

(7) The 2,6-dimethylnaphthalene crystals are allowed to warm to room temperature, and if desired, any melted material is removed.

The 2,7-dimethylnaphthalene concentrate which is removed from crystallizer **39** is passed through line **41** into isomerizer **42**. In isomerizer **42** a catalytic isomerization reaction effects a transfer of a substantial portion of the β-alkyl groups to the α position. Thus, 2,7-dimethylnaphthalene is converted into a mixture containing 2,6- and 2,7-dimethylnaphthalenes. It should be noted, however, that this isomerization reaction does not effect any shift of alkyl groups from one of the aryl rings to the other in the same molecule although some amount of disproportionation between separate molecules may occur. Although the 2,7-dimethylnaphthalene is substantially converted to the 2,6-isomer, other α-methylnaphthalenes, such as 1,5-, 1,6-, 1,7- and 1,8- isomers may also be obtained.

One manner of effecting the isomerization in isomerizer **42** is to contact the 2,7-dimethylnaphthalene with any solid, acidic, cracking catalyst, such as silica-alumina, silica-magnesia, silica-zirconia and acid-activated clays. The reaction temperature should be in the range of 300°–500° C., and preferably 400°–450° C. The liquid space velocity can vary between 0.1 and 20 volumes of hydrocarbon per volume of catalyst per hour and more preferably is maintained in the range of 0.5–6. It is desirable to conduct the isomerization at a low pressure, generally in the range of 0.05–0.5 atmosphere, as otherwise coking tends to occur rapidly with resultant deactivation of the catalyst. The low pressure can be maintained either by holding a vacuum on isomerizer **42** or by introducing an inert diluent along with the 2,7-dimethylnaphthalene, e.g., nitrogen, hydrogen, methane, propane, butanes, and the like. Whenever the activity of the catalyst has dropped enough to require regeneration, this can be done in conventional manner merely by flowing air through the hot catalyt to burn off the coke deposits. Thereafter the catalyst can be re-used for further isomerization.

Depending upon the conditions chosen for operating the isomerization reaction, the isomerizate removed from isomerizer **42** via line **43** is recycled in either of two ways. In one embodiment, if the isomerization conditions are chosen so that the isomerizate in line **43** contains, for all practical purposes, only an equilibrium mixture of 2,6- and 2,7-dimethylnaphthalenes, the isomizate is recycled through lines **50** and **38** into crystallizer **39** in said second crystallization zone for separation of additional 2,6-dimethylnaphthalene. Alternately in another embodiment, if the isomerization conditions in isomerizer **42** are chosen so that substantial amounts of other dialkyl isomers are obtained, then the isomerizate is passed via line **44** through line **23** into crystallizer **25** in said first crystallization zone wherein additional 2,6- and 2,7-dimethylnaphthalenes are obtained.

I claim:

1. In a process involving,

(1) hydrodesulfurizing a petroleum fraction boiling mainly in the range of 440°–525° F. and containing mainly monocyclic and dicyclic aromatic hydrocarbons including dimethylnaphthalenes,

(2) separating from the desulfurization product material containing alkylnaphthalenes,

(3) subjecting such material to a dealkylation reaction at a temperature above 1000° F. to produce naphthalene and,

(4) recovering from the dealkylation product naphthalene and a fraction rich in monoalkylnaphthalene, the steps for producing and recovering 2,6-dimethylnaphthalene which comprises:

(a) separating from the hydrodesulfurization product a fraction boiling essentially in the range of 500°–510° F.,

(b) fractionally crystallizing in a first crystallization zone the 500°–510° F. fraction to separate 2,6- and 2,7-dimethylnaphthalene from other dimethylnaphthalenes,

(c) passing the filtrate from step (b), materials from step (a) boiling below 500° F. and above 510° F., and said fraction rich in monoalkylnaphthalene to said dealkylation reaction for conversion to naphthalene,

(d) fractionally crystallizing in a second crystallization zone the 2,6- and 2,7-dimethylnaphthalene product from step (b) to separate the 2,6-dimethylnaphthalene from the 2,7-dimethylnaphthalene,

(e) recovering the 2,6-dimethylnaphthalene,

(f) isomerizing the 2,7-dimethylnaphthalene from step (d) to a mixture rich in 2,6- and 2,7-dimethylnaphthalene, and,

(g) recovering 2,6-dimethylnaphthalene from said mixture.

2. Process according to claim 1 wherein said mixture from step (f) is recycled to said first crystallization zone.

3. Process according to claim 1 wherein said mixture from step (f) is recycled to said second crystallization zone.

4. In a process involving,

(1) hydrodesulfurizing a petroleum fraction boiling mainly in the range of 440°–525° F. and containing mainly monocyclic and dicyclic aromatic hydrocarbons including dimethylnaphthalenes,

(2) separating from the desulfurization product material containing alkylnaphthalenes,

(3) subjecting such material to a dealkylation reaction at a temperature above 1000° F. to produce naphthalene and,

(4) recovering from the dealkylation product naphthalene and a fraction rich in monoalkylnaphthalene, the steps for producing and recovering 2,6-dimethylnaphthalene which comprises:

(a) separating from the hydrodesulfurization product a fraction boiling essentially in the range of 500°–510° F.,

(b) fractionally crystallizing in a first crystallization zone the 500°–510° F. fraction to separate 2,6- and 2,7-dimethylnaphthalene from other dimethylnaphthalenes,

(c) passing the filtrate from step (b), materials

from step (a) boiling below 500° F. and above 510° F., and said fraction rich in monoalkylnaphthalene to said dealkylation reaction for conversion to naphthalene,

(d) fractionally crystallizing in a second crystallization zone the 2,6- and 2,7-dimethylnaphthalene product from step (b) to separate the 2,6-dimethylnaphthalene from the 2,7-dimethylnaphthalene,

(e) recovering the 2,6-dimethylnaphthalene,

(f) isomerizing the 2,7-dimethylnaphthalene from step (d) to a mixture rich in 2,6-dimethylnaphthalene by contacting said 2,7-dimethylnaphthalene with a solid, acidic, cracking catalyst, selected from the group consisting of silica-alumina, silica-magnesia, silica-zirconia and acid-activated clays at a temperature in the range of 300°–500° C., a pressure in the range of 0.05–0.5 atmosphere, and a liquid hourly space velocity between 0.1 and 20 volumes of hydrocarbon per volume of catalyst per hour, and,

(g) recovering 2,6-dimethylnaphthalene from said mixture.

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