

**METHOD OF MAKING 2,6-DIMETHYLNAPHTHALENE
FROM OTHER DIMETHYLNAPHTHALENE ISOMERS AND FROM
DIMETHYLTETRALINS/DIMETHYLDECALINS
WITH A METHYL GROUP ON EACH RING**

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FIELD OF THE INVENTION

The present invention relates to a method for making
2,6-dimethylnaphthalene from a hydrocarbon feed comprising isomers of
10 dimethylnaphthalene (DMN) and dimethyltetralins/dimethyldecalins
(DMT/DMD) having a methyl group on each ring.

BACKGROUND OF THE INVENTION

15 There are ten different isomers of dimethylnaphthalene (DMN). Of these,
nine of them can be grouped into three triads based on the relative ease of
isomerization within a certain triad. Such an intra-triad isomerization can be
done using a wide variety of solid acids as catalysts. This ease of
isomerization within a triad is based on the fact that a methyl group on
20 naphthalene shifts relatively easily from an alpha position to a beta position or
vice versa on the same ring but does not shift easily from a beta position to
another beta position on the same ring or from an alpha position to another
alpha position. The three triad groups are as follows: 2,7-, 1,7- and
1,8-dimethylnaphthalene; 2,6-, 1,6- and 1,5-dimethylnaphthalene; and 1,4-,
25 1,3- and 2,3-dimethylnaphthalene. 1,2-dimethylnaphthalene is the tenth
isomer and doesn't fit into any of the three triads.

Although isomerization of dimethylnaphthalenes within these triad groups is
relatively easy, isomerization from one triad group to another triad group is
30 much more difficult. Since certain of the isomers of dimethylnaphthalene are
much more valuable than others for use in plastics synthesis, investigators

are continually making attempts to find ways of converting from less useful to more useful isomers. A particularly valuable isomer is 2,6-dimethylnaphthalene. Certain processes for synthesizing dimethylnaphthalenes result in high yields of 2,7- and

5 1,7-dimethylnaphthalenes. Conversion of 2,7- and 1,7-dimethylnaphthalenes into 2,6-dimethylnaphthalene has been accomplished using certain zeolites such as ZSM-5. However, such conversion has resulted in an excess of undesirable side products such as methylnaphthalenes, trimethylnaphthalenes and 1,4-, 1,3- and 2,3-dimethylnaphthalene via

10 dealkylation, cracking and transalkylation. Usually, this acid-catalyzed isomerization is associated with catalyst deactivation as the reaction goes on, resulting in a short catalyst life.

It would be very useful to find an economical way to convert 2,7- and

15 1,7-dimethylnaphthalene which occur as abundant products in dimethylnaphthalene synthesis to 2,6-dimethylnaphthalene in a high yield.

Other investigators have found methods of converting the dimethylnaphthalene isomers, particularly 2,7-dimethylnaphthalene to the

20 most useful, and therefore most valuable isomer, 2,6-dimethylnaphthalene, but none of these conversion methods have been sufficiently simple and economical to warrant the general use of such methods.

U.S. Patent No. 3,890,403 (Shimada et al.) discloses a method which can

25 reportedly be used to obtain 2,6-dimethylnaphthalene from a dimethylnaphthalene mixture containing the various isomers of dimethylnaphthalene. The method involves (a) partially hydrogenating the dimethylnaphthalene mixture to obtain dimethyltetralins (DMT) with a hydrogenation catalyst such as nickel, platinum, palladium, rhodium, copper-

30 chromium, iridium or ruthenium; (b) isomerizing the dimethyltetralins with a solid acid catalyst such as a zeolite catalyst so that the dimethyltetralin

isomers in which the two methyl groups occur on the same ring can be converted to the dimethyltetralin isomers in which the two methyl groups occur on opposite rings and the amount of dimethyltetralin isomers in which the two methyl groups occur on opposite rings is brought near to thermodynamical equilibrium; (c) separating and collecting the dimethyltetralin isomers in which the two methyl group occur on opposite rings from the isomers in which the two methyl groups occur on the same ring; (d) dehydrogenating the collected DMT mixture to convert it into a DMN mixture; (e) separating and recovering 2,6-DMN from the recovered DMN mixture. Although this method obtains the desirable 2,6-DMN isomer from other DMN isomers, the method is quite time-consuming and expensive because it involves several quite separate and distinct steps.

U.S. Patent No. 3,803,253 (Suld) discloses a process of hydroisomerization/dehydrogenation of a mixture of dimethylnaphthalenes, so that 2,6-dimethylnaphthalene can be obtained and isolated out from the reaction mixture. The other remaining products are then recycled and the process is repeated to obtain more 2,6-dimethylnaphthalene. The catalyst used for the hydroisomerization/dehydrogenation step is described as a combination of a calcium-containing faujasite and a hydrogenation/dehydrogenation catalyst component. The process step, with hydroisomerization and dehydrogenation performed simultaneously in the same reaction vessel in the presence of the described combination catalyst, simplifies the process but makes the overall efficiency and yield of the process quite low.

U.S. Patent No. 3,928,482 (Hedge et al.), which is related to '253 discussed above, discloses a hydroisomerization process by which 2,6-DMT is obtained from a feed mixture which is rich in 2,7- or 1,7-DMT using an aluminosilicate zeolite containing polyvalent metal cations in exchange positions. This process is intended to be incorporated as an improvement to the method of

'253 discussed above but does not overcome the basic lack of success of that process for obtaining 2,6-DMN in high yields in a cost-effective way.

- An economical method of obtaining 2,6-DMN from other DMN isomers, especially isomers in the 2,7-DMN triad, with few steps and at relatively high yields is needed. The present inventors have found such a method.

SUMMARY OF THE INVENTION

- 10 One object of the present invention is to provide an economical method of making 2,6-dimethylnaphthalene in relatively high and stable yields.

- Another object of the present invention is to provide a method of utilizing a dimethylnaphthalene isomer or mixture of isomers selected from the group
15 consisting of 1,6-dimethylnaphthalene, 1,5-dimethylnaphthalene, 2,7-dimethylnaphthalene, 1,7-dimethylnaphthalene, 1,8-dimethylnaphthalene and partially or fully hydrogenated counterparts thereof to produce 2,6-dimethylnaphthalene.

- 20 Still another object of the present invention is to provide a method of making 2,6-dimethylnaphthalene with no significant formation of naphthalene, methylnaphthalenes, trimethylnaphthalenes and 1,4-, 1,3-, 2,3- and 1,2-dimethylnaphthalene.

- 25 Yet another object of the present invention is to provide a method of making 2,6-dimethylnaphthalene using a two-step hydroisomerization/dehydrogenation process.

- An additional object of the present invention is to provide a method of making
30 2,6-dimethylnaphthalene using a two-step hydroisomerization/dehydrogenation process in conjunction with an intra-triad

isomerization process in which 1,7- and 1,8-DMN are converted on an acid catalyst to 2,7-DMN and 1,6- and 1,5-DMN are converted on an acid catalyst to 2,6-DMN, respectively, the 2,6-DMN is separated out and the 2,7-DMN is then converted to 2,6-DMN with the hydroisomerization/dehydrogenation
5 process.

Another object of the present invention is to provide a method of utilizing an acid catalyst in a hydroisomerization step followed by a reforming or dehydrogenation catalyst in a dehydrogenation step to convert
10 2,7-dimethylnaphthalene triad isomers (especially 2,7- and 1,7-DMN) to 2,6-dimethylnaphthalene triad isomers (especially 2,6- and 1,6-DMN).

Other features and advantages of the invention will be apparent from the following description.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph plotting the yields of DMT and DMD products resulting from the hydroisomerization run of 2,7-DMN at 400°F versus the time-on-stream at which the products were analyzed on-line as described in
20 Example 6.

Figure 2 is a graph plotting the conversion of 2,7-DMN and yields of various products resulting from an acid-catalyzed isomerization of 2,7-DMN on
25 H-ZSM-11 versus the time-on-stream, as described in Example 11. Figure 3 is a similar graph plotting the conversion and selectivities versus the time-on-stream when the resulting 1,5-, 1,6- and 1,7-DMN as well as the unconverted 2,7-DMN are assumed to be recycled and finally converted to 2,6-DMN.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to a method of making 2,6-dimethylnaphthalene. Specifically, the invention relates to a method of using dimethylnaphthalene isomer or mixture of isomers selected from the group consisting of 1,6-dimethylnaphthalene, 1,5-dimethylnaphthalene, 2,7-dimethylnaphthalene, 1,7-dimethylnaphthalene, 1,8-dimethylnaphthalene, and partially or fully hydrogenated counterparts thereof to obtain 2,6-dimethylnaphthalene. The invention also relates to using an acid catalyst (the catalyst's acidity being measured by the catalyst's positive adsorption of ammonia, pyridine, and piperidine probes on its surface sites) with a metal in a hydroisomerization step followed by a reforming catalyst in a dehydrogenation step to obtain 2,6-dimethylnaphthalene from a dimethylnaphthalene isomer or mixture of isomers selected from the group consisting of 1,6-dimethylnaphthalene, 1,5-dimethylnaphthalene, 2,7-dimethylnaphthalene, 1,7-dimethylnaphthalene, 1,8-dimethylnaphthalene, and partially or fully hydrogenated counterparts thereof. The invention further relates to the use of a metal with an acid catalyst. This can be any metal that is effective as a catalyst in hydrogenation reactions, such as, for example, palladium, nickel, copper or platinum. In another preferred embodiment, the acid catalyst is used with a metal in a range of from 0.1 to 30 weight %. In one preferred embodiment, the metal used with the acid catalyst is palladium. In another preferred embodiment, the metal used with the acid catalyst is platinum. In yet another preferred embodiment, the metal is sulfided. Non-limiting examples of hydroisomerization catalysts which can be used are PdS/Boron-Beta (in the presence of 500 ppm aluminum), PtS/Boron-Beta (in the presence of 500 ppm aluminum), PdS/Y, and non-sulfided Pd/Boron-Beta (in the presence of 500 ppm aluminum). PtS/Boron-SSZ-33 is not as effective as a hydroisomerization catalyst because of its tendency to serve only a hydrogenating function and not to isomerize the various DMN isomers to the 2,6-DMD or -DMT isomer.

A possible mechanism for the process of obtaining 2,6-dimethylnaphthalene from 2,7-, 1,7-, 1,8-, 1,5- and 1,6-dimethylnaphthalene with the acid catalyst and the noble metal could relate to dimethylnaphthalenes being partially or fully saturated to dimethyltetralins or dimethyldecalins on or in the catalyst.

- 5 According to this possible mechanism, once at least one of the aromatic rings in dimethylnaphthalenes is saturated, the beta-beta migration of methyl groups becomes much easier because the energy barriers for such a migration are lifted by changing the reaction pathways. It appears, according to this mechanism, that if there is sufficient acidity on or in the catalyst, the
- 10 saturated DMN's will isomerize near to equilibrium.

- After the above hydroisomerization, the saturated dimethylnaphthalenes must be reformed back to unsaturated dimethylnaphthalenes by dehydrogenation. For this step to work with high selectivity, i.e., avoiding
- 15 non-2,6-dimethylnaphthalenes, the reforming step should be done over a catalyst which avoids transalkylation, dealkylation, and cracking reactions. In a preferred embodiment, catalysts that can be used in the reforming step are both acidic and non-acidic catalysts. A non-limiting example of an acidic catalyst that can be used is a mixture of rhenium and platinum on alumina
- 20 (sulfided Pt/Re/Al₂O₃). Non-limiting examples of a non-acidic catalyst that can be used are sulfided Pt/Na-ZSM-5 and PtS/Cs/Boron-SSZ-42.

- An alternative method of obtaining 2,6-DMN from other DMN isomers, particularly those in the 2,7-DMN triad, is by means of an acid-catalyzed DMN
- 25 isomerization. Unlike the hydroisomerization/dehydrogenation two-step process discussed above, this process proceeds in one step and does not involve the partially or fully saturated intermediate DMT and/or DMD forms. A non-limiting example of a catalyst that can be used for such an acid-catalyzed isomerization is H-ZSM-11. This process is less preferred than the
- 30 hydroisomerization/dehydrogenation process discussed above because it has a tendency to produce a fair amount of methylnaphthalenes (MN) and

trimethylnaphthalenes (TMN) as well as the undesired isomers of DMN. Thus, its yield of 2,6-DMN is low in comparison to the hydroisomerization/dehydrogenation process.

- 5 In all the embodiments of the hydroisomerization/dehydrogenation process, the dimethylnaphthalene feed (neat or in solution) can be flowed over the catalyst along with hydrogen gas or the reaction can be performed batchwise. In this process, the temperature needs to be high enough to hydrogenate the dimethylnaphthalene feed and to isomerize the resulting DMD's and DMT's.
- 10 The hydroisomerization reaction depends on both the hydrogenation/dehydrogenation activity and acid strength of the catalyst. Additionally, in order to generate a significant amount of DMT/DMD's, the hydrogen pressure needs to be sufficiently high. Thermodynamically, higher temperatures drive the equilibrium towards DMN while higher hydrogen
- 15 pressures help shift the equilibrium towards the saturated species (DMD). The reaction kinetics, which are dependent on the catalyst type, also have a strong influence on the product selectivity in relation to the hydrogenation/dehydrogenation activity and acid strength of the catalyst. In a preferred embodiment, the yield of partially saturated species (DMT) from the
- 20 hydroisomerization reaction should be at least 5 weight percent. In a more preferred embodiment, the yield of partially saturated species (DMT) should be at least 10 weight percent. Accordingly, the Weight Hourly Space Velocity (WHSV) can be varied over a broad range (e.g., about 0.1 to 100 h⁻¹), the pressure can vary from 0 to 3000 psig, the hydrogen/hydrocarbon molar ratio
- 25 can vary from ~0.0 to 100, and the reactor temperature can vary from about 300 to 1000°F. The unreacted material and the partially hydrogenated products other than 2,6-isomers can be recycled back to the reactor or reformed back to DMN's in a separate reactor. Various product separation schemes can be used at different points of the process. Also, in one
- 30 embodiment, a more conventional isomerization process to interconvert isomers within triads can be used in conjunction with this process.

In both the hydroisomerization and the reforming step, there are many variables to be optimized. These include: run temperature, pressure, space velocity, and the catalyst itself. As shown below, when such variables are optimized, approximately 50% conversion of 2,7- to 2,6-triad can be achieved.

- 5 The resulting non-2,6-DMN C₁₂-isomers can be separated from 2,6-DMN product and recycled to the hydroisomerization reactor to be further converted to 2,6-DMN, boosting the 2,6-DMN production. Furthermore, little or no formation of 1,2-DMN, 1,3-DMN, 1,4-DMN, 2,3-DMN or TMN is encountered. There is also relatively little formation of MN's with the isomerization catalysts
- 10 used. By taking measures to minimize hydrogenolysis during the isomerization reaction, such as by adding a little sulfur to the feed, formation of MN's can be minimized even further. With such results achieved with the present invention, it is now possible to achieve large scale isomerization of 2,7-, 1,7-, 1,8-, 1,5- and 1,6-DMN to 2,6-DMN. In addition, the yield of
- 15 2,6-DMN can be also increased through enhancing the DMN feedstocks by incorporating the more conventional, acid-catalyzed intra-triad isomerization of DMN's into the hydroisomerization/dehydrogenation process. Such intra-triad isomerization of DMN's may be further associated with a recycling step described above.

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- In experiments described below, various hydroisomerization catalysts were used. In these experiments, there was little evidence of deactivation of the catalysts, in some cases after up to approximately three weeks of continuous use. It was also found in these experiments that the reforming step converted
- 25 almost all of the saturated species back to DMN's. In fact, a ratio of ~95/5 DMN/saturated species or better can be achieved if the various conditions are optimized.

EXAMPLES

The present invention will be further described with the following tables and figures showing the results of several experiments.

5

Hydrogenation without Isomerization

The results of Examples 1-4 with PtS/Boron-SSZ-33 reveal that effective hydroisomerization of DMN's to DMT's requires not only a sufficient
10 hydrogenation/dehydrogenation function such as that of PtS but also a sufficient acidity since PtS/Boron-SSZ-33 tends to serve only a hydrogenating function and not to isomerize the resulting DMT's to other DMT isomers.

Taking advantage of these results, the DMT isomers (1,5-, 1,6-, 2,5-, 1,7-,
15 2,8- and 2,7-DMT) produced in Examples 1-4, together with 1,4- and 2,6-DMT which are supplied as standards by Chemsampco and API/Carnegie Mellon University, respectively, are used to identify and quantify the major DMT isomers produced in the hydroisomerization step of this invention (see Example 8) on an expanded scale. It is beneficial to have the major DMD's
20 and DMT's, especially DMT's, identified in the hydroisomerization step since it roughly gives the information on how much 2,6-isomers can be produced, useful for the prediction of 2,6-DMN yield even prior to the reforming step to be conducted after the hydroisomerization.

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Example 1

Hydrogenation of 1,5-DMN with PtS/B-SSZ-33

An experiment was performed to hydrogenate a hydrocarbon feed of 5:1 (wt:wt) o-xylene:1,5-dimethylnaphthalene in a reactor with a
30 PtS/Boron-SSZ-33 catalyst (0.5 g). The reaction was conducted at 400°F, 200 psig, 1 ml/hr feed and 40 ml/min H₂. 96% of 1,5-DMN was converted,

yielding 88% 1,5-DMT and 8% DMD's and other C12's. No other DMT isomers are observed. The identification of the GC peaks was confirmed by GC/MS analysis. In this example and the examples which follow, the diluent o-xylene and its reaction products are subtracted out of the yield data shown in the tables.

Example 2

Hydrogenation of 1,6-DMN with PtS/B-SSZ-33

10 An experiment was performed to hydrogenate a hydrocarbon feed of 5:1 (wt:wt) o-xylene:1,6-dimethylnaphthalene in a reactor with a PtS/Boron-SSZ-33 catalyst (0.5 g). The reaction was conducted at 420°F, 200 psig, 0.5 ml/hr feed and 40 ml/min H₂. Depending on which aromatic ring of 1,6-DMN is hydrogenated, two different DMT isomers were produced, 15 namely, 1,6-DMT and 2,5-DMT. Basically, no other DMT's were present in the product. At 100% conversion of 1,6-DMN, 31% 1,6-DMT and 23% 2,5-DMT were yielded with other 46% as DMD's and other C12 species. The identification of the GC peaks was confirmed by GC/MS analysis.

Example 3

Hydrogenation of 1,7-DMN with Pts/B-SSZ-33

20 An experiment was performed to hydrogenate a hydrocarbon feed of 5:1 (wt:wt) o-xylene:1,7-dimethylnaphthalene in a reactor with a PtS/Boron-SSZ-33 catalyst (0.5 g). The reaction was conducted at 420°F, 25 200 psig, 0.5 ml/hr feed and 40 ml/min H₂. Depending on which aromatic ring of 1,7-DMN is hydrogenated, two different DMT isomers were produced, namely, 1,7-DMT and 2,8-DMT. Basically, no other DMT's were present in the product. At ~100% conversion of 1,7-DMN, 26% 1,7-DMT and 28% 30 2,8-DMT were yielded with the other 46% as DMD's and other C12 species. The identification of the GC peaks was confirmed by GC/MS analysis.

Example 4Hydrogenation of 2,7-DMN with PtS/B-SSZ-33

An experiment was performed to hydrogenate a hydrocarbon feed of 5:1
5 (wt:wt) o-xylene:2,7-dimethylnaphthalene in a reactor with a
PtS/Boron-SSZ-33 catalyst (0.5 g). The reaction was conducted at 380°F,
200 psig, 1 ml/hr feed, and 40 ml/min H₂. At 100% conversion of 2,7-DMN,
2,7-DMT yield was 75%. Other 25% are DMD's and other C₁₂'s. No other
DMT isomers are observed. The identification of the GC peaks is confirmed
10 by GC/MS analysis.

Hydroisomerization without Dehydrogenation

Examples 5-10 describe the results of experiments performing the
15 hydroisomerization step without a subsequent dehydrogenation of the
hydroisomerization products.

Example 5Hydroisomerization of 2,7-DMN with PdS/Y

20 Three experiments were performed to hydroisomerize a hydrocarbon feed of
5:1 (wt:wt) o-xylene:2,7-dimethylnaphthalene in a reactor with PdS/Y to
produce DMT's and DMN's at 420, 400 and 350°F, respectively. Other
conditions were 200 psig, 1 ml/hr feed, 40 ml/min H₂ and 0.5 g catalyst. The
25 compositions of the products are given in weight % in Table V. No
methylnaphthalenes were detected. Essentially no cracking products were
observed.

Table V

Temperature (°F)	420	400	350
DMN's	3.1	2.9	2.6
DMD's + other C12's	33.2	23.5	9.0
DMT's (total)	63.7	73.6	88.4
1,5-DMT	0.4	0.2	0
1,6-DMT	1.8	1.1	0.2
2,5-DMT	4.6	3.6	0.9
1,7-DMT	2.1	1.8	1.1
2,8-DMT	4.3	3.8	1.3
2,7-DMT	29.8	45.3	78.9
2,6-DMT	20.1	17.4	5.8
1,4-DMT	0	0	0
Other DMT's	0.6	0.4	0.2

Example 6Hydroisomerization of 2,7-DMN with PdS/Y

- 5 Four experiments were performed to hydroisomerize a hydrocarbon feed of 5:1 (wt:wt) o-xylene:2,7-dimethylnaphthalene in a reactor with PdS/Y at 500 psig, 1 ml/hr feed, 40 ml/min H₂ and 0.5 g catalyst. The reaction temperature was 380, 400, 420 and 440°F, respectively. The compositions of the products are given in weight % in Table VI. No methylnaphthalenes were
- 10 detected. Essentially no cracking products were observed. Figure 1 demonstrates the DMT and DMD yields versus the reaction time for the run at 400°F. After an initial period of about 70 hours, the catalyst activity and selectivity became stable. For the next two weeks, this catalyst in the same reactor was uninterruptedly screened under various conditions with various
- 15 feeds containing various DMN isomers. The results indicate no apparent deactivation of the catalyst.

Table VI

Temperature (°F)	440	420	400	380
DMN's	1.9	1.3	0.3	0.2
DMD's + other C12's	38.3	34.4	31.1	19.9
DMT's (total)	59.8	64.3	68.6	79.9
1,5-DMT	1.1	0.8	0.3	0.1
1,6-DMT	3.5	3.0	1.3	1.0
2,5-DMT	6.5	6.5	6.0	4.4
1,7-DMT	3.5	3.1	1.5	1.5
2,8-DMT	6.3	6.5	5.9	4.8
2,7-DMT	18.8	23.3	33.4	49.5
2,6-DMT	17.7	19.6	20.1	18.6
1,4-DMT	0	0	0	0
Other DMT's	2.4	1.5	0.1	0

Example 7Hydroisomerization of 2,7-DMN with PdS/Y

- 5 Three experiments were performed to hydroisomerize a hydrocarbon feed of 5:1 (wt:wt) o-xylene:2,7-dimethylnaphthalene in a reactor with PdS/Y at 500 psig, 2 ml/hr feed, 40 ml/min and 0.5 g catalyst. The reaction temperature was 400, 420 and 440°F, respectively. The compositions of the products are given in weight % in Table VII. No methylnaphthalenes were
- 10 detected. Essentially no cracking products were observed.

Table VII

Temperature (°F)	440	420	400
DMN's	1.4	1.0	1.7
DMD's + other C12's	22.5	12.2	7.5
DMT's (total)	76.1	86.8	90.8
1,5-DMT	0.9	0.4	0.2
1,6-DMT	2.9	1.7	0.9
2,5-DMT	8.7	7.0	4.3
1,7-DMT	2.9	1.9	1.7
2,8-DMT	8.3	7.1	4.7
2,7-DMT	26.3	42.3	61.0
2,6-DMT	24.4	26.0	17.8
1,4-DMT	0	0	0
Other DMT's	1.7	0.4	0.2

Example 8Hydroisomerization of 2,7-DMN with Pd/B/Al/Beta

5 An experiment was performed to isomerize a hydrocarbon feed of 5:1 (wt:wt) o-xylene:2,7-dimethylnaphthalene in a reactor with a Pd/Boron-Beta catalyst (0.5 g) containing 500 ppm aluminum. The reaction conditions were: 475°F, 200 psig, 1 ml/hr feed, 40 ml/min H₂. 89.2% of the product was DMT's. 8.7% of the product was DMD's and others. 2.1% of the product was DMN's.

10

Example 9Hydroisomerization of 2,7-DMN with PdS/SAPO-11

15 Several experiments were made to hydroisomerize a hydrocarbon feed of 5:1 (wt:wt) o-xylene:2,7-dimethylnaphthalene in a reactor with a PdS/SAPO-11 (0.5 g) with 40 ml/min H₂ at a feed rate of 1 ml/hr. The results are shown in weight % in Tables IXa-IXc.

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TABLE IXa

	Experiment 1	Experiment 2	Experiment 3	Experiment 4
Temperature (°F)	650	600	500	650
Pressure (psig)	200	200	200	100
WHSV (h ⁻¹)	2	2	2	2
DMD's	13.0	45.2	100	14.2
DMT's	34.5	34.4		19.3
DMN (total)	52.0	20.4		65.9
2,7-DMN	24.9	11.1		46.5
1,7-DMN	6.2	1.9		6.1
1,8-DMN	0	0		0
2,6-DMN	14.5	5.7		10.5
1,6-DMN	6.2	1.6		2.7
1,5-DMN	0.2	0.1		0.1
1,3-DMN	0	0		0
2,3-DMN	0	0		0
1,4-DMN	0	0		0
1,2-DMN	0	0		0
MN's	~0.5	~0.6		~0.3
TMN's	0	0		~0.1

DMN: dimethylnaphthalene; DMT: dimethyltetralin; DMD: dimethyldecalin;

5 MN: methylnaphthalene; TMN: trimethylnaphthalene.

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TABLE IXb

	Experiment 5	Experiment 6	Experiment 7	Experiment 8
Temperature (°F)	700	725	725	725
Pressure (psig)	200	200	150	150
WHSV (h ⁻¹)	6	6	6	6
DMD's	2.1	1.4	0.3	trace
DMT's	20.3	13.7	8.3	~9
DMN (total)	77.2	84.4	90.9	90.5
2,7-DMN	50.5	55.0	~70	~70
1,7-DMN	9.6	14.6	15.4	15.4
1,8-DMN	0	0	0	0
2,6-DMN	13.2	9.7	~3	~3
1,6-DMN	3.8	4.8	2.4	2.0
1,5-DMN	0.1	0.3	0.1	0.1
1,3-DMN	0	0	0	0
2,3-DMN	0	0	0	0
1,4-DMN	0	0	0	0
1,2-DMN	0	0	0	0
MN's	~0.3	~0.5	~0.4	~0.3
TMN's	~0.1	0	~0.1	0

TABLE IXc

	Experiment 9	Experiment 10	Experiment 11	Experiment 11 (reanalyzed)
Temperature (°F)	725	725	775	775
Pressure (psig)	150	150	150	150
WHSV (h ⁻¹)	12	2	2	2
DMD's	Trace	trace	trace	0.7
DMT's	~8	8.0	5.2	4.6
DMN (total)	93.0	92.0	93.6	93.7
2,7-DMN	~80	55.5	45.5	44.7
1,7-DMN	~12	21.3	31.7	32.1
1,8-DMN	0	0	0	0
2,6-DMN	Trace	8.4	8.2	8.9
1,6-DMN	~1	6.5	7.4	7.5
1,5-DMN	0	0.3	0.8	0.5
1,3-DMN	0	0	0	0
2,3-DMN	0	0	0	0
1,4-DMN	0	0	0	0
1,2-DMN	0	0	trace	0
MN's	0	trace	~0.9	0.9
TMN's (wt.%)	0	0	0.3	0.1

Example 10

5 GC/MS Analysis of Products of Hydroisomerization of 2,7-DMN with
PdS/SAPO-11

Gas chromatography coupled with mass spectrometry was used to identify the products from a particular yield period (Experiment 5 in Example 9). The composition of the products from Experiment 5 at 700°F, 200 psig, 6 h⁻¹ WHSV is listed in weight % in Tables Xa and Xb. The difference between the compositions determined by on-line GC (see Table IXb) and off-line GC/MS (see Tables Xa and Xb) is apparently due to the different sensitivity of these two different analytical techniques.

TABLE Xa

DMD's	C ₃ I's	DMT's	MN's	C ₆ Bz + C ₅ Tol
2.3	3.4	21.0	0.6	0.8

DMN: dimethylnaphthalene; DMT: dimethyltetralin; DMD: dimethyldecalin;
 MN: methylnaphthalene; C₃I: indan substituted with a C₃ alkyl group; C₆Bz:
 5 benzene substituted with a C₆ alkyl group; C₅Tol: toluene substituted with a
 C₅ alkyl group.

TABLE Xb

2,7-DMN	1,7-DMN	2,6-DMN	1,6-DMN	1,5-DMN
~45.5	10.5	~11	4.2	0.2

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Acid Catalyst Isomerization without Hydrogenation

Example 11 shows the results of an experiment in which an acid catalyst is
 used without combining it with a hydrogenating catalyst.

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Example 11Isomerization of 2,7-DMN with H-ZSM-11

An experiment was performed to isomerize a hydrocarbon feed of 5:1 (wt:wt)
 o-xylene:2,7-dimethylnaphthalene in a reactor with an acid catalyst,
 H-ZSM-11 with no carrier gas at 600°F, ~5 psig, 1 ml/hr feed and 0.2 h⁻¹

20 WHSV. The results are shown in graphic form in Figure 2. Assuming that the
 resulting 1,5-, 1,6- and 1,7-DMN as well as the unconverted 2,7-DMN are
 recyclable and can be finally converted to 2,6-DMN, the selectivities of the
 desirable 2,6-DMN and other major by-products such as MN's and TMN's
 then can be depicted as shown in Figure 3. It is apparent that this kind of
 25 acid-catalyzed DMN isomerization results in a significant amount of

by-products such as MN's (methylnaphthalenes) and TMN's (trimethylnaphthalenes) that can be depicted as shown in Figure 3.

Hydroisomerization/Dehydrogenation

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Examples 12-25 describe experiments in which product of the hydroisomerization step is then dehydrogenated with a separate catalyst.

Example 12

10 Hydroisomerization/Dehydrogenation of 2,7-DMN with PdS/SAPO-11 and PtS/Cs/B-SSZ-42

Experiments were conducted using a two-reactor hydroisomerization/dehydrogenation system. The first reactor facilitates the hydroisomerization function and the second reactor performs the function of dehydrogenating saturated compounds back to DMN's. In the first reactor, a PdS/SAPO-11 catalyst (0.5 g) was used. In the second reactor, a PtS/Cs/Boron-SSZ-42 (0.45 g) catalyst was used. Tables XIIa and XIIb show results from using the two reactor system. The feed was composed of o-xylene and 2,7-DMN in a 5:1 (wt:wt) ratio.

TABLE XIIa

	Experiment 1		Experiment 2	
	Reactor 1	Reactor 2	Reactor 1	Reactor 2
Temperature, °F	650	750	650	795
Pressure, psig	200	~5	200	~5
Feed Rate, ml/hr	1	1	1	1
H ₂ Rate, ml/min	40	40	40	40
C ₅ -	<1	~0	<1	~0
DMD's	12.7	3.2	12.0	2.1
DMT's, C ₃ I's, MN's	38.2	4.8	38.2	4.7
DMN's (total)	48.1	92.0	48.8	93.2
2,7-DMN		68.7		69.2
1,7-DMN		8.1		8.5
2,6-DMN		12.6		12.6
1,6-DMN		2.6		2.5
1,5-DMN		~0		~0
Other DMN's		~0		~0

DMN: dimethylnaphthalene; DMT: dimethyltetralin; DMD: dimethyldecalin;

MN: methylnaphthalene; C₃I: indan substituted with a C₃ alkyl group.

TABLE XIIb

	Experiment 3		Experiment 4	
	Reactor 1	Reactor 2	Reactor 1	Reactor 2
Temperature, °F	650	900	725	800
Pressure, psig	200	~5	400	~5
Feed Rate, ml/hr	1	1	0.5	0.5
H ₂ Rate, ml/min	40	40	30	30
C ₅ -	<1	~0	~5	~0
DMD's	11.1	0.6	14.9	5.3
DMT's, C ₃ I's, MN's	39.0	5.2	39.6	22.7
DMN's (total)	48.9	94.2	40.3	72.0
2,7-DMN		70.2		32.2
1,7-DMN		9.0		12.7
2,6-DMN		12.4		17.1
1,6-DMN		2.6		10.0
1,5-DMN		~0		~0
Other DMN's		~0		~0

Example 13

GC/MS Analysis of Products of Hydroisomerization/Dehydrogenation
of 2,7-DMN with PdS/SAPO-11 and PtS/Cs/B-SSZ-42

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Gas chromatography (GC) coupled with mass spectrometry (MS) was used to identify the products from particular yield periods (shown in Example 12) after Reactor 2. The distributions of different non-DMN's in the non-DMN products are listed in weight % in Table XIII based on the GC/MS results.

Table XIII

	Experiment 1	Experiment 2	Experiment 3	Experiment 4
MI's	--	1.9	9.1	--
EI's	--	--	4.8	0.8
DMD's	39.5	30.8	9.4	19.0
DMT's	28.3	29.1	6.8	34.1
MEI's	3.5	3.8	--	--
MEI ⁺ 's	11.0	12.3	17.2	13.6
MN's	10.1	14.8	43.8	6.1
C ₅ Tol's	7.6	7.3	8.9	24.9
EN's	--	--	--	1.5

MI: methylindan; EI: ethylindan; DMD: dimethyldecalin; DMT: dimethyltetralin; MEI: methylethylindan; MEI⁺: methylethylindene; MN: methylnaphthalene; C₅Tol: toluene substituted with a C₅ alkyl group; EN: ethylnaphthalene.

Example 14

Hydroisomerization/Dehydrogenation of 2,7-DMN with Pd/B/Al/Beta and PtS/Cs/B-SSZ-42

Experiments were conducted using a two-reactor hydroisomerization/dehydrogenation system. The first reactor facilitates the hydroisomerization function and the second reactor performs the function of dehydrogenating saturated compounds back to DMN's. In the first reactor, a Pd/Boron/500 ppm Al/beta catalyst (0.5) was used. In the second reactor, a PtS/Cs/Boron-SSZ-42 (0.45 g) catalyst was used. Table XIV shows results for the example. In this example, the feed was composed of o-xylene and 2,7-DMN of a 5:1 wt:wt ratio. The slightly high yield of MN's after reactor 2 is likely related to the dealkylation of the resulting DMN's on PtS/Cs/B-SSZ-42.

Table XIV

	Experiment 1		Experiment 2		Experiment 3	
	Reactor 1	Reactor 2	Reactor 1	Reactor 2	Reactor 1	Reactor 2
Temperature, °F	535	850	500	850	475	850
Pressure, psig	200	~5	200	~5	200	~5
Feed Rate, ml/hr	1	1	1	1	1	1
H ₂ Rate, ml/min	40	40	40	40	40	40
C ₅ 's	1.8	-	~0.6	-	<0.3	-
DMD's	20.1	12.4	13.7	4.3	9.6	1.7
DMT's, C ₃ l's	72.7	17.2	84.2	4.2	89.4	2.0
MN's	~0	3.3	~0	3.0	~0	3.7
DMN's (total)	5.4	67.1	1.5	86.9	0.7	92.6
2,7-DMN		21.0		32.1		41.3
1,7-DMN		11.3		10.2		6.9
2,6-DMN		20.6		31.1		34.4
1,6-DMN		13.0		12.8		10.0
1,5-DMN		0.9		0.4		-
Other DMN's		0.3		0.3		-

DMN: dimethylnaphthalene; DMT: dimethyltetralin; DMD: dimethyldecalin;
 MN: methylnaphthalene; C₃l: indan substituted with a C₃ alkyl group.

Example 15Hydroisomerization/Dehydrogenation of 2,7-DMN with Pd/B/Al/Beta
and PtS/Cs/B-SSZ-42

- Further experiments were conducted using a two-reactor
- 5 hydroisomerization/dehydrogenation system similar to Example 14. The first reactor facilitates the hydroisomerization function and the second reactor performs the function of dehydrogenating saturated compounds back to DMN's. In the first reactor, a Pd/Boron/500 ppm Al/beta catalyst (0.5 g) was used. In the second reactor, a PtS/Cs/Boron-SSZ-42 (0.45 g) catalyst was
- 10 used. Table XV shows results for the example. In this example, the feed was composed of o-xylene and 2,7-DMN of a 5:1 wt:wt ratio. As described in Example 14, the slightly high yield of MN's after reactor 2 is likely related to the dealkylation of the resulting DMN's on PtS/Cs/B-SSZ-42.

Table XV

	Experiment 1		Experiment 2	
	Reactor 1	Reactor 2	Reactor 1	Reactor 2
Temperature, °F	475	850	475	850
Pressure, psig	200	~5	200	~5
Feed Rate, ml/hr	1.3	1.3	1.1	1.1
H ₂ Rate, ml/min	40	40	40	40
C ₅ -	<1	-	-	-
DMD's	5.0	0.9	2.7	0.8
DMT's, C ₃ I's	94.2	1.5	96.3	2.0
MN's	~0	2.5	~0	5.3
DMN's (total)	0.7	95.1	<1	91.9
2,7-DMN		51.5		42.4
1,7-DMN		4.8		6.7
2,6-DMN		32.0		33.4
1,6-DMN		6.8		9.4
1,5-DMN		~0		~0
Other DMN's		~0		~0

- 15 DMN: dimethylnaphthalene; DMT: dimethyltetralin; DMD: dimethyldecalin; MN: methylnaphthalene; C₃I: indan substituted with a C₃ alkyl group.

Example 16GC/MS Analysis of Products of Hydroisomerization/Dehydrogenation
of 2,7-DMN with Pd/B/Al/Beta and PtS/Cs/B-SSZ-42

Gas chromatography coupled with mass spectrometry was used to identify some of the products obtained from Example 15 described. The product from Experiment 1 of Example 15 was collected from Reactor 1 only and is designated in this example as Experiment A. The product from Experiment 2 of Example 15 was collected from both Reactors 1 and 2 and is designated in this example as Experiment B. The results of the identification of the products from both experiments in weight % are shown in Table XVI. The difference between the compositions determined by GC (see Table XV of Example 15) and GC/MS (see Table XVI of this example) is apparently due to the different sensitivities of these two different analytical techniques.

15

Table XVI

	Experiment A (reactor 1 only)	Experiment B (reactors 1+2)
N (naphthalene)	0	0.2
MI's (methylindeans)	0	0.2
EI's (ethylindans) or DMI's (dimethylindeans)	0	0.3
DMD's (dimethyldecalins)	13.5	1.4
DMT's (dimethyltetralins)	78.1	2.7
MEI's (methylethylindans) or TMI's (trimethylindans)	4.5	0.2
MEI's (methylethylindenenes)	0	0
MN's (methylnaphthalenes)	0	7.0
C ₅ Tol's (C ₅ -toluenes)	1.0	0
EN's (ethylnaphthalenes)	0	0.2
DMN's (dimethylnaphthalenes)	2.5	87.1
TMT's (trimethyltetralins)	0.4	0
TMN's (trimethylnaphthalenes)	0	0.7

Example 17Hydroisomerization/Dehydrogenation of 2,7-DMN with PdS/Siral 40
and PtS/Cs/B-SSZ-42

Experiments were conducted using a two-reactor

- 5 hydroisomerization/dehydrogenation system. The first reactor facilitates the hydroisomerization function and the second reactor performs the function of dehydrogenating saturated compounds back to DMN's. In the first reactor, a PdS/Siral 40 catalyst, consisting of sulfided Pd deposited on commercial Siral 40 silica-alumina (0.5 g), was used. In the second reactor, a
- 10 PtS/Cs/Boron-SSZ-42 (0.45 g) catalyst was used. Tables XVIIa and XVIIb show results in weight % for the experiments. In these experiments, the feed was composed of o-xylene and 2,7-DMN in a 5:1 (wt:wt) ratio.

Table XVIIa

	Experiment 1		Experiment 2	
	Reactor 1	Reactor 2	Reactor 1	Reactor 2
Temperature, °F	550	850	500	850
Pressure, psig	200	~5	200	~5
Feed Rate, ml/hr	1	1	1	1
H ₂ Rate, ml/min	40	40	40	40
C ₅ -	~1.2	-	~0.7	-
DMD's	55.8	22.5	42.9	13.4
DMT's, C ₃ I's	38.8	13.2	54.7	6.7
MN's	~0	2.6	~0	3.7
DMN's (total)	4.1	61.7	1.7	76.2
2,7-DMN		28.5		39.2
1,7-DMN		5.5		8.1
2,6-DMN		18.6		19.5
1,6-DMN		6.7		8.4
1,5-DMN		0.5		0.5
Other DMN's		1.9 (2,3- & 1,2-DMN)		0.5 (2,3- & 1,2-DMN) (also 0.3 TMN's)

- 15 DMN: dimethylnaphthalene; DMT: dimethyltetralin; DMD: dimethyldecalin;
MN: methylnaphthalene; C₃I: indan with a C₃ alkyl group;
TMN: trimethylnaphthalene.

Table XVIIb

	Experiment 3		Experiment 4	
	Reactor 1	Reactor 2	Reactor 1	Reactor 2
Temperature, °F	500	850	475	850
Pressure, psig	200	~5	200	~5
Feed Rate, ml/hr	1	1	1	1
H ₂ Rate, ml/min	40	40	40	40
C ₅ -	~0.3	--	~0.4	--
DMD's	28.9	7.7	27.0	5.5
DMT's, C ₃ I's	69.4	2.0	71.8	1.4
MN's	~0	4.2	~0	5.1
DMN's (total)	1.4	86.1	0.8	88.0
2,7-DMN		47.9		59.4
1,7-DMN		7.1		4.7
2,6-DMN		24.6		19.6
1,6-DMN		6.5		4.1
1,5-DMN		-		0.2
Other DMN's		-		trace

Example 18

Hydroisomerization/dehydrogenation of 2,7-DMN with Pd/B/Al/Beta
and PtS/Na-ZSM-5

5

In Example 8, a hydrocarbon feed of 5:1 (wt:wt)
 o-xylene:2,7-dimethylnaphthalene was hydroisomerized in a reactor with a
 Pd/Boron/Al/Beta catalyst (0.5 g) containing 500 ppm aluminum at 475°F and
 10 200 psig. The hydroisomerization products including the solvent o-xylene
 were collected and then dehydrogenated by being subjected as feed to
 PtS/Na-ZSM-5 in a reactor at 850°F, 100 psig, 0.5 ml/hr feed, 23 ml/min H₂
 and 0.5 g catalyst. The compositions of the feed for the dehydrogenation
 reaction (hydroisomerization products of 2,7 DMN in Example 8) and its
 15 dehydrogenation product are shown in weight % in Table XVIII.

Table XVIII

	2,7-DMN (used as feed for hydro- isomerization)	Feed for dehydrogenation (made from 2,7-DMN hydro- isomerization)	Product of dehydrogenation
DMN's (total)	100	2.1	94.2
2,7-DMN	100	0.9	50.1
2,6-DMN	0	0.6	27.5
1,7-DMN	0	0.2	7.3
1,6-DMN	0	0.2	9.1
1,5-DMN	0	0.1	0.2
other DMN's	0	0.1	0
DMD's + other C12's	0	8.7	1.7
DMT's (total)	0	89.2	4.1
1,5-DMT	0	0.1	0
1,6-DMT	0	2.4	0.1
2,5-DMT	0	6.2	0.2
1,7-DMT	0	2.4	0.1
2,8-DMT	0	4.5	0.2
2,7-DMT	0	43.7	1.7
2,6-DMT	0	29.2	1.0
1,4-DMT	0	0	0
Other DMT's	0	0.7	0.8
MN's	0	0	0

Example 19

5 Hydroisomerization/dehydrogenation of 2,7-DMN with PdS/Y and PtS/Na-
ZSM-5

In Example 6, a hydrocarbon feed of 5:1 (wt:wt)
o-xylene:2,7-dimethylnaphthalene was hydroisomerized in a reactor with
10 PdS/Y (0.5 g) catalyst at 400°F and 500 psig. The hydroisomerization
products including the solvent o-xylene were collected and then

dehydrogenated by being subjected as feed to PtS/Na-ZSM-5 in a reactor at 850°F, 100 psig, 0.5 ml/hr feed, 23 ml/min H₂ and 0.5 g catalyst. The compositions of the feed (hydroisomerization products of 2,7-DMN in Example 6) and its dehydrogenation product are shown in weight % in Table XIX. The dehydrogenation catalyst was stable under these condition for at least 9 days.

Table XIX

	2,7-DMN (used as feed for hydro- isomerization)	Feed for dehydrogenation (made from 2,7-DMN hydro- isomerization)	Product of dehydrogenation
DMN's (total)	100	0.3	94.8
2,7-DMN	100	0.1	52.7
2,6-DMN	0	0.1	22.3
1,7-DMN	0	0.1	9.7
1,6-DMN	0	0	8.9
1,5-DMN	0	0	0.9
Other DMN's	0	0	0.3
DMD's + other C12's	0	31.1	1.0
DMT's (total)	0	68.6	1.6
1,5-DMT	0	0.3	0
1,6-DMT	0	1.3	0.1
2,5-DMT	0	6.0	0.1
1,7-DMT	0	1.5	0.1
2,8-DMT	0	5.9	0.1
2,7-DMT	0	33.4	0.4
2,6-DMT	0	20.1	0.3
1,4-DMT	0	0	0
Other DMT's	0	0.1	0.5
MN's	0	0	2.6

Example 20Hydroisomerization/dehydrogenation of 2,7-DMN with PdS/Y and
PtS/Re/Al₂O₃

- 5 A hydrocarbon feed of 5:1 (wt:wt) o-xylene:2,7-dimethylnaphthalene was hydroisomerized in a reactor with PdS/Y catalyst at 350-475°F, 200 psig, 1.0 ml/hr feed, 40 ml/min H₂ and 0.5 g catalyst. The hydroisomerization product including the solvent o-xylene was collected and then dehydrogenated by being fed to a sulfided Pt/Re/Al₂O₃ catalyst (0.3 wt. % Pt,
- 10 0.3 wt. % Re, 1.1 wt. % Cl on Al₂O₃) in a reactor at 850°F, 100 psig, 0.3 ml/hr feed, 23 ml/min H₂ and 0.5 g catalyst. It appears that due to the acidic properties of Pt/Re/Al₂O₃ catalyst a significant amount of methylnaphthalenes were produced as by-products in the dehydrogenation step when Pt/Re/Al₂O₃ was used as dehydrogenation catalyst. The compositions of the 2,7-DMN
- 15 feed (for the hydroisomerization), the dehydrogenation feed (hydroisomerization products of 2,7-DMN) and the dehydrogenation product are shown in weight % in Table XX.

Table XX

	2,7-DMN (used as feed for hydro- isomerization)	Feed for dehydrogenation (made from 2,7-DMN hydro- isomerization)	Product of dehydrogenation
DMN's (total)	100	0.8	85.3
2,7-DMN	100	0.4	27.5
2,6-DMN	0	0.2	15.9
1,7-DMN	0	0.1	22.3
1,6-DMN	0	0.1	16.4
1,5-DMN	0	0	2.9
Other DMN's	0	0	0.3
DMD's + other C12's	0	32.5	2.7
DMT's (total)	0	66.7	~0
1,5-DMT	0	0.2	~0
1,6-DMT	0	1.4	~0
2,5-DMT	0	3.4	~0
1,7-DMT	0	1.9	~0
2,8-DMT	0	3.5	~0
2,7-DMT	0	42.7	~0
2,6-DMT	0	13.5	~0
1,4-DMT	0	0	~0
Other DMT's	0	0.1	~0
1-MN	0	0	3.5
2-MN	0	0	8.3
TMN's	0	0	0.2

Example 21

Hydrogenation/dehydrogenation of 1,5-DMN
with PtS/B-SSZ-33 and PtS/Na-ZSM-5

5

In Example 1, a hydrocarbon feed of 5:1 (wt:wt)
o-xylene:1,5-dimethylnaphthalene was hydrogenated in a reactor with a

PtS/Boron-SSZ-33 catalyst (0.5 g) at 400°F and 200 psig. The hydrogenation products including the solvent o-xylene were collected and then dehydrogenated by being fed to PtS/Na-ZSM-5 in a reactor at 850°F, 100 psig, 0.5 ml/hr feed, 23 ml/min H₂ and 0.5 g catalyst. As described in

5 Example 1, in the hydrogenation step, 96% of 1,5-DMN was converted, yielding 88% 1,5-DMT and 8% DMD's and other C₁₂'s. No other DMT isomers were observed. In the dehydrogenation step of this example, the resulting dehydrogenation product has the following composition: ~0% DMD's and other C₁₂'s, 0.9% 1,5-DMT, 1.3% other DMT's, 96.5% 1,5-DMN,

10 1.3% 1,6/1,7-DMN. No MN's were detected. Since PtS/Na-ZSM-5 works for the "bulky" 1,5-isomers as demonstrated in this example, this catalyst apparently also works for the dehydrogenation of other DMN isomers.

Example 22

15 Hydroisomerization/dehydrogenation of 1,5-DMN with PdS/Y and
PtS/Na-ZSM-5

A hydrocarbon feed of 5:1 (wt:wt) o-xylene:1,5-dimethylnaphthalene was hydroisomerized in a reactor with a PdS/Y catalyst at 440°F, 500 psig,

20 0.5 ml/hr feed, 40 ml/min H₂ and 0.5 g catalyst. The hydroisomerization products including the solvent o-xylene were collected and then dehydrogenated by being fed to a PtS/Na-ZSM-5 in a reactor at 850°F, 100 psig, 0.5 ml/hr feed, 23 ml/min H₂ and 0.5 g catalyst. The compositions of the 1,5-DMN feed (for the hydroisomerization), the dehydrogenation feed

25 (hydroisomerization products of 1,5-DMN), and the dehydrogenation product are shown in weight % in Table XXII.

Table XXII

	1,5-DMN (used as feed for hydro- isomerization)	Feed for dehydrogenation (made from 1,5-DMN hydro- isomerization)	Product of dehydrogenation
DMN's (total)	100	2.6	81.7
2,7-DMN	0	0.7	12.9
2,6-DMN	0	0.6	13.3
1,7-DMN	0	0.3	20.9
1,6-DMN	0	0.2	26.3
1,5-DMN	100	0.1	7.9
Other DMN's	0	0.7	0.4
DMD's + other C12's	0	26.2	7.5
DMT's (total)	0	70.8	5.6
1,5-DMT	0	6.5	0.2
1,6-DMT	0	14.3	0.1
2,5-DMT	0	6.7	0.1
1,7-DMT	0	12.7	0.2
2,8-DMT	0	4.7	0.1
2,7-DMT	0	9.7	0.1
2,6-DMT	0	10.7	0.2
1,4-DMT	0	0	0
Other DMT's	0	5.5	4.6
1-MN	0	0	2.2
2-MN	0	0	2.0
TMN's	0	0.4	1.0

Example 23Hydroisomerization/dehydrogenation of 1,6-DMNwith PdS/Y and PtS/Na-ZSM-5

- 5 A hydrocarbon feed of 5:1 (wt:wt) o-xylene:1,6-dimethylnaphthalene was hydroisomerized in a reactor with PdS/Y catalyst at 440°F, 500 psig, 0.5 ml/hr feed, 40 ml/min H₂ and 0.5 g catalyst. The hydroisomerization products including the solvent o-xylene were collected and then dehydrogenated by being subjected as feed to a PtS/Na-ZSM-5 in a reactor at 850°F, 100 psig,
- 10 0.5 ml/hr feed, 23 ml/min H₂ and 0.5 g catalyst. The compositions of the 1,6-DMN feed (for the hydroisomerization), the dehydrogenation feed (hydroisomerization products of 1,6-DMN) and the dehydrogenation product are shown in weight % in Table XXIII.

Table XXIII

	1,6-DMN (used as feed for hydro- isomerization)	Feed for dehydrogenation (made from 1,6-DMN hydro- isomerization)	Product of dehydrogenation
DMN's (total)	100	2.2	86.8
2,7-DMN	0	0.5	11.0
2,6-DMN	0	0.3	16.9
1,7-DMN	0.7	0.3	18.7
1,6-DMN	98.0	0.5	33.8
1,5-DMN	0.7	0.1	5.8
Other DMN's	0.6	0.5	0.6
DMD's + other C12's	0	10.4	2.7
DMT's (total)	0	86.4	4.7
1,5-DMT	0	5.6	0.1
1,6-DMT	0	17.8	0.1
2,5-DMT	0	13.9	0.1
1,7-DMT	0	11.9	0.1
2,8-DMT	0	5.7	0.1
2,7-DMT	0	10.0	0.1
2,6-DMT	0	16.6	0.6
1,4-DMT	0	0	0
Other DMT's	0	4.9	3.5
1-MN	0	0	1.7
2-MN	0	0	1.7
TMN's	0	1.0	2.4

Example 24Hydroisomerization/dehydrogenation of 1,7-DMN
with PdS/Y and PtS/Na-ZSM-5

- 5 A hydrocarbon feed of 5:1 (wt:wt) o-xylene:1,7-dimethylnaphthalene was hydroisomerized in a reactor with PdS/Y catalyst at 440°F, 500 psig, 0.5 ml/hr feed, 40 ml/min H₂ and 0.5 g catalyst. The hydroisomerization products including the solvent o-xylene were collected and then dehydrogenated by being fed to PtS/Na-ZSM-5 in a reactor at 850°F, 100 psig, 1.0 ml/hr feed,
- 10 23 ml/min H₂ and 0.5 g catalyst. The compositions of the 1,7-DMN feed (for the hydroisomerization), the dehydrogenation feed (hydroisomerization products of 1,7-DMN), and the dehydrogenation product are shown in weight % in Table XXIV.

Table XXIV

	1,7-DMN (used as feed for hydro- isomerization)	Feed for dehydrogenation (made from 1,7-DMN hydro- isomerization)	Product of dehydrogenation
DMN's (total)	100	2.4	78.4
2,7-DMN	0	0.5	20.2
2,6-DMN	0	0.4	17.0
1,7-DMN	100	0.2	19.4
1,6-DMN	0	0.2	18.2
1,5-DMN	0	0.1	3.0
Other DMN's	0	1.0	0.6
DMD's + other C12's	0	40.4	10.0
DMT's (total)	0	57.2	5.6
1,5-DMT	0	2.3	0.2
1,6-DMT	0	7.1	0.1
2,5-DMT	0	5.7	0.2
1,7-DMT	0	6.9	0.2
2,8-DMT	0	5.5	0.2
2,7-DMT	0	12.4	0.2
2,6-DMT	0	12.6	0.3
1,4-DMT	0	0	0
Other DMT's	0	4.7	4.2
1-MN	0	0	1.9
2-MN	0	0	2.8
TMN's	0	0	1.3

Example 25Hydroisomerization/dehydrogenation of a DMN mixture
with PdS/Y and PtS/Na-ZSM-5

- 5 A hydrocarbon feed of 5:1 (wt:wt) o-xylene:DMN mixture (approximately 2,7-DMN:1,7-DMN:1,6-DMN:1,5-DMN = 2:2:2:1 by weight) was hydroisomerized in a reactor with PdS/Y catalyst at 420°F, 500 psig, 1.0 ml/hr feed, 40 ml/min H₂ and 0.5 g catalyst. The hydroisomerization products including the solvent o-xylene were collected and then dehydrogenated by
- 10 being fed to PtS/Na-ZSM-5 in a reactor at 850°F, 100 psig, 1.0 ml/hr feed, 23 ml/min H₂ and 0.5 g catalyst. The compositions of the DMN mixture feed (for the hydroisomerization), the dehydrogenation feed (hydroisomerization products of DMN mixture), and the dehydrogenation product are shown in weight % in Table XXV.

Table XXV

	DMN mixture (used as feed for hydro- isomerization)	Feed for dehydrogenation (made from DMN mixture hydro- isomerization)	Product of dehydrogenation
DMN's (total)	100	1.5	87.8
2,7-DMN	28.3	0.4	23.2
2,6-DMN	0	0.3	18.3
1,7-DMN	28.7	0.1	20.4
1,6-DMN	28.4	0.1	21.0
1,5-DMN	14.6	0.1	4.0
Other DMN's	0	0.5	0.9
DMD's + other C12's	0	45.1	6.3
DMT's (total)	0	53.4	2.1
1,5-DMT	0	2.2	0.1
1,6-DMT	0	6.8	0.1
2,5-DMT	0	5.5	0.1
1,7-DMT	0	6.6	0.2
2,8-DMT	0	5.1	0.1
2,7-DMT	0	12.1	0.2
2,6-DMT	0	12.1	0.3
1,4-DMT	0	0	0
Other DMT's	0	3.0	1.0
1-MN	0	0	1.3
2-MN	0	0	1.9
TMN's	0	0	0.6

Although a few embodiments of the invention have been described in detail
5 above, it will be appreciated by those skilled in the art that various
modifications and alterations can be made to the particular embodiments
shown without materially departing from the novel teachings and advantages
of the invention. Accordingly, it is to be understood that all such modifications
and alterations are included within the spirit and scope of the invention as
10 defined by the following claims.

**WHAT IS CLAIMED IS:**

1. A method of making 2,6-dimethylnaphthalene comprising:
 - (a) contacting a hydrocarbon feed comprising a dimethylnaphthalene isomer or mixture of isomers selected from the group consisting of 1,6-dimethylnaphthalene, 1,5-dimethylnaphthalene, 2,7-dimethylnaphthalene, 1,7-dimethylnaphthalene, 1,8-dimethylnaphthalene, and partially or fully hydrogenated counterparts thereof with an acidic catalyst in the presence of hydrogen gas to obtain a hydroisomerized mixture comprising 2,6-dimethyltetralin, 2,6-dimethyldecalin; and
 - (b) contacting the hydroisomerized mixture with a reforming catalyst to dehydrogenate the hydroisomerized mixture thus obtaining a dehydrogenated mixture comprising 2,6-dimethylnaphthalene.
2. The method of Claim 1 further comprising recycling through step (a) and step (b) hydrocarbons other than 2,6-dimethylnaphthalene, 2,6-dimethyldecalin, and 2,6-dimethyltetralin from the hydroisomerized mixture produced in step (a) and/or hydrocarbons other than 2,6-dimethylnaphthalene from the dehydrogenated mixture of step (b) to yield additional 2,6-DMN.
3. The method of Claim 1 further comprising contacting the feed mixture before and/or after step (a) with an acidic catalyst under conditions sufficient to maximize production of 2,6-DMN through intra-triad isomerization of DMN.
4. The method of Claim 1 wherein the feed mixture is neat or in solution.



5. The method of Claim 1 wherein the weight hourly space velocity is in a range from 0.1 to 100 hr⁻¹.
6. The method of Claim 1 wherein the molar ratio of hydrogen to hydrocarbon in step (a) is in a range from 0.1 to 100.
- 5 7. The method of Claim 1 wherein step (a) is conducted at a temperature in a range from 300°F to 1000°F.
8. The method of Claim 1 wherein the catalyst in step (a) is selected from the group consisting of oxides of silica, boron, aluminum, gallium, germanium, iron, chromium, zirconium and mixtures thereof.
- 10 9. The method of Claim 8 wherein the catalyst in step (a) further comprises a noble metal.
10. The method of Claim 9 wherein the noble metal is in a range from 0.1 to 10% by weight of the catalyst in step (a).
11. The method of Claim 9 wherein the noble metal is selected from the
15 group consisting of palladium and platinum.
12. The method of Claim 8 wherein the catalyst in step (a) is selected from the group consisting of amorphous materials and zeolitic materials.
13. The method of Claim 12 wherein the catalyst in step (a) is selected from the group consisting of SAPO-11, Al/B/beta catalyst, Y zeolite and
20 amorphous silica-aluminum catalyst.
14. The method of Claim 1 wherein the catalyst in step (b) comprises a catalyst which is substantially non-acidic.



15. The method of Claim 14 wherein the non-acidic catalyst in step (b) is selected from the group consisting of Pt/Na-ZSM-5 and Pt/Cs/B-SSZ-42.
16. The method of Claim 14 wherein the non-acidic catalyst in step (b) is sulfided.
- 5 17. The method of Claim 1 wherein the catalyst in step (b) comprises an acidic reforming catalyst.
18. The method of Claim 17 wherein the acidic reforming catalyst in step (b) is Pt/Re on alumina.
- 10 19. A method of using non-2,6-dimethylnaphthalene to obtain 2,6-dimethylnaphthalene comprising:
- (a) contacting a hydrocarbon feed comprising a dimethylnaphthalene isomer or mixture of isomers selected from the group consisting of 1,6-dimethylnaphthalene, 1,5-dimethylnaphthalene, 2,7-dimethylnaphthalene, 1,7-dimethylnaphthalene, 15 1,8-dimethylnaphthalene, and partially or fully hydrogenated counterparts thereof with an acidic catalyst in the presence of hydrogen gas to obtain a hydroisomerized mixture comprising 2,6-dimethyldecalin and 2,6-dimethyltetralin; and
- (b) 20 contacting the hydroisomerized mixture with a reforming catalyst to dehydrogenate the hydroisomerized mixture, thus obtaining a dehydrogenated mixture comprising 2,6-dimethylnaphthalene.
20. The method of Claim 19 further comprising recycling through step (a) and step (b) hydrocarbons other than 2,6-dimethylnaphthalene, 2,6-dimethyldecalin, and 2,6-dimethyltetralin from the hydroisomerized 25 mixture produced in step (a) and/or hydrocarbons other than



2,6-dimethylnaphthalene from the dehydrogenated mixture of step (b) to yield additional 2,6-DMN.

- 5 21. The method of Claim 19 further comprising contacting the feed mixture before and/or after step (a) with an acidic catalyst under conditions sufficient to maximize production of 2,6-DMN and 2,7-DMN through intra-triad isomerization of DMN.
22. The method of Claim 19 wherein the feed mixture is neat or in solution.
23. The method of Claim 19 wherein the weight hourly space velocity is in a range from 0.1 to 100 hr⁻¹.
- 10 24. The method of Claim 19 wherein the molar ratio of hydrogen to hydrocarbon in step (a) is in a range from 0.1 to 100.
25. The method of Claim 19 wherein step (a) is conducted at a temperature in a range from 300°F to 1000°F.
- 15 26. The method of Claim 20 wherein the catalyst in step (a) is selected from the group consisting of oxides of silica, boron, aluminum, gallium, germanium, iron, chromium, zirconium and mixtures thereof.
27. The method of Claim 26 wherein the catalyst in step (a) further comprises a noble metal.
- 20 28. The method of Claim 27 wherein the noble metal is in a range from 0.1 to 10% by weight of the catalyst of the catalyst in step (a).
29. The method of Claim 27 wherein the noble metal is selected from the group consisting of palladium and platinum.



30. The method of Claim 26 wherein the catalyst in step (a) is selected from the group consisting of amorphous materials and zeolitic materials.
31. The method of Claim 30 wherein the catalyst in step (a) is selected from the group consisting of SAPO-11, Al/B/beta catalyst, Y zeolite and amorphous silica-aluminum catalyst.
32. The method of Claim 19 wherein the catalyst in step (b) comprises a non-acidic catalyst.
33. The method of Claim 32 wherein the non-acidic catalyst in step (b) is selected from the group consisting of Pt/Na-ZSM-5 and Pt/Cs/B-SSZ-42.
34. The method of Claim 33 wherein the non-acidic catalyst in step (b) is sulfided.
35. The method of Claim 19 wherein the catalyst in step (b) comprises an acidic reforming catalyst.
36. The method of Claim 35 wherein the acidic reforming catalyst in step (b) is Pt/Re on alumina.
37. A method of using an acidic catalyst in a hydroisomerization step followed by a non-acidic reforming catalyst in a dehydrogenation step to obtain 2,6-dimethylnaphthalene from a dimethylnaphthalene isomer or mixture of isomers selected from the group consisting of 1,6-dimethylnaphthalene, 1,5-dimethylnaphthalene, 2,7-dimethylnaphthalene, 1,7-dimethylnaphthalene, 1,8-dimethylnaphthalene, and partially or fully hydroisomerized counterparts thereof comprising:
- (a) contacting a hydrocarbon feed comprising a dimethylnaphthalene isomer or mixture of isomers selected from the group consisting of



5 1,6-dimethylnaphthalene, 1,5-dimethylnaphthalene,
2,7-dimethylnaphthalene, 1,7-dimethylnaphthalene,
1,8-dimethylnaphthalene, and partially or fully hydrogenated
counterparts thereof with an acidic catalyst in the presence of
hydrogen gas to obtain a hydroisomerized mixture comprising
2,6-dimethyldecalin and 2,6 dimethyltetralin; and

(b) contacting the hydroisomerized mixture with a reforming catalyst to
dehydrogenate the hydroisomerized mixture thus obtaining a
dehydrogenated mixture comprising 2,6-dimethylnaphthalene.

10 38. The method of Claim 37 further comprising recycling through step (a)
and step (b) hydrocarbons other than 2,6-dimethylnaphthalene,
2,6-dimethyldecalin, and 2,6-dimethyltetralin from the hydroisomerized
mixture produced in step (a) and/or hydrocarbons other than
15 2,6-dimethylnaphthalene from the dehydrogenated mixture of step (b) to
yield additional 2,6-DMN.

39. The method of Claim 37 further comprising contacting the feed mixture
before and/or after step (a) with an acidic catalyst under conditions
sufficient to maximize production of 2,6-DMN through intra-triad
isomerization of DMN.

20 40. The method of Claim 37 wherein the hydrocarbon feed is neat or in
solution.

41. The method of Claim 37 wherein the hydrocarbon feed in step (a) is
flowed at a weight hourly space velocity in a range from 0.1 to 100 hr⁻¹.

25 42. The method of Claim 37 wherein the molar ratio of hydrogen to
hydrocarbon in step (a) is in a range from 0.1 to 100.



43. The method of Claim 37 wherein step (a) is conducted at a temperature in a range from 300°F to 1000°F.
44. The method of Claim 37 wherein the catalyst in step (a) is selected from a group consisting of oxides of silica, boron, aluminum, gallium,
5 germanium, iron, chromium, zirconium and mixtures thereof.
45. The method of Claim 37 wherein the catalyst in step (a) further comprises a noble metal.
46. The method of Claim 45 wherein the noble metal is in a range from 0.1 to 10% by weight of the catalyst in step (a).
- 10 47. The method of Claim 45 wherein the noble metal is selected from the group consisting of palladium and platinum.
48. The method of Claim 44 wherein the catalyst in step (a) is selected from the group consisting of amorphous materials and zeolitic materials.
49. The method of Claim 48 wherein the catalyst in step (a) is selected from
15 the group consisting of SAPO-11, Al/B/beta catalyst, Y zeolite and amorphous silica-aluminum catalyst.
50. The method of Claim 37 wherein the catalyst in step (b) comprises a non-acidic catalyst.
51. The method of Claim 50 wherein the non-acidic catalyst in step (b) is
20 selected from the group consisting of Pt/Na-ZSM-5 and Pt/Cs/B-SSZ-42.
52. The method of Claim 51 wherein the non-acidic catalyst in step (b) is sulfided.



53. The method of Claim 37 wherein the catalyst in step (b) comprises an acidic reforming catalyst.
54. The method of Claim 53 wherein the acidic reforming catalyst in step (b) is Pt/Re on alumina.