

**METHOD FOR PRODUCING 2,6-DMN FROM MIXED
DIMETHYLNAPHTHALENES BY CRYSTALLIZATION,
ADSORPTION AND ISOMERIZATION**

FIELD OF THE INVENTION

The invention relates to a process for the separation of 2,6-DMN from other DMN isomers and conversion of non-2,6-DMN isomers into the desired 2,6-DMN product.

BACKGROUND OF THE INVENTION

2,6-DMN is an intermediate produced during the manufacture of 2,6-naphthalene dicarboxylic acid (2,6-NDA) and 2,6-naphthalene dicarboxylate (2,6-NDC). 2,6-NDA and 2,6-NDC are monomers either of which, when combined with ethylene glycol, reacts to make polyethylene naphthalate (PEN), a polyester with unique and advantageous commercial applications in films, fibers, and packaging.

The isomers of dimethylnaphthalene are difficult to separate from one another by distillation because their boiling points are very similar. Technology exists to recover 2,6-DMN by crystallization, or by adsorption, or by adsorption followed by crystallization. It is difficult to separate 2,6-DMN from 2,7-DMN by crystallization alone because they form a eutectic. It is expensive to recover 2,6-DMN from mixed DMNs by adsorption alone because there are no known materials that selectively adsorb 2,6-DMN. In previous technology, when adsorption and crystallization steps were combined, the adsorption step was always used to remove the majority of the undesired DMN isomers. Furthermore, the adsorption step was often followed by an additional crystallization step to obtain the desired product purity.



166166



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-2-

1 An additional complication in the commercial production of 2,6-DMN is the
2 difficulty of converting DMN isomers other than 2,6-DMN into the desired
3 2,6-DMN isomer. It is well known that during DMN isomerization, it is easy to
4 move methyl groups on a naphthalene ring when they migrate from an alpha
5 position (i.e., 1, 4, 5 or 8) to a beta position (i.e., 2, 3, 6 or 7) or *vice versa*, but
6 it is difficult when the methyl groups must rearrange from one beta position to
7 another. DMN isomers have been classified into groups called "triads" within
8 which isomerization is readily accomplished. These triads are (1) 1,5-DMN,
9 1,6-DMN, and 2,6-DMN; (2) 1,7-DMN, 1,8-DMN, and 2,7-DMN; and
10 (3) 1,3-DMN, 1,4-DMN, and 2,3-DMN. The tenth isomer, 1,2-DMN, consists
11 of two methyl groups in adjacent alpha and beta positions and does not fall
12 into one of the aforementioned triads.

13

14 Producers have developed methods for making commercial quantities of
15 2,6-DMN by avoiding co-producing the 2,7-DMN isomer because of the
16 difficulty in recovering 2,6-DMN at high yield in the presence of 2,7-DMN.
17 Furthermore, producers have tried to avoid making isomers outside the
18 2,6-triad because of the difficulty in isomerizing across triads. Isomers that
19 cannot be converted to 2,6-DMN represent a yield loss and inefficient use of
20 raw materials. Additionally, adsorption is not practical when the concentration
21 of 2,6-DMN in the feed stream is low because there are no known materials
22 that will preferentially adsorb 2,6-DMN over the other isomers. These
23 limitations often necessitate the use of expensive raw materials and
24 controlled organic synthesis reactions that can produce only isomers in the
25 2,6-triad, such as alkylation of butadiene and ortho-xylene, and methylation of
26 methylnaphthalene.

27 Technologies relating to the purification of 2,6-DMN from DMN isomer
28 mixtures by crystallization, adsorption and distillation are known as are
29 technologies relating to the isomerization of non-2,6-DMN to 2,6-DMN.

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-3-

1 Separation of DMN isomers by crystallization is relatively straightforward if the
2 feed composition is quite high in 2,6-DMN isomer, or if a low yield is
3 acceptable, or if the feed to be crystallized consists of isomers within a triad.
4 If the concentration of 2,6-DMN is well above the eutectic composition, simple
5 crystallization can produce pure 2,6-DMN in high yields. If the concentration
6 of 2,6-DMN is slightly above the eutectic composition, low yield of high purity
7 DMN can be obtained. If the mixture consists of isomers within the 2,6-DMN
8 triad, the unrecovered material, a mixture of 1,5-DMN, 1,6-DMN and
9 2,6-DMN, can be easily isomerized to produce a mixture with 2,6-DMN above
10 the eutectic composition. Crystallization alone becomes insufficient to purify
11 mixed DMNs to make 2,6-DMN when both the 2,6-DMN and 2,7-DMN
12 isomers are present because they form a eutectic.

13

14 The feasibility of adsorption separation for DMN isomers has been
15 demonstrated. However, no material has been published that selectively
16 adsorbs 2,6-DMN from a feed of mixed DMN's. This limitation makes it
17 expensive to recover 2,6-DMN from mixed DMNs by adsorption alone
18 because the adsorption equipment must be very large in order to remove all
19 components other than 2,6-DMN from a feed stream that contains small
20 quantities of 2,6-DMN.

21

22 One technique for overcoming the limitations of 2,6-DMN purification by
23 crystallization or by adsorption is to combine the two technologies. Such a
24 combination has always previously been done by using the adsorption step as
25 a feed pretreatment step prior to the crystallization step.

26

27 An alternative technique to break the 2,6-DMN/2,7-DMN eutectic is to partially
28 or completely saturate the naphthalene ring. The resulting decalins or
29 tetralins do not form a eutectic at the same composition as the
30 dimethylnaphthalenes, so an incremental quantity of the 2,6- and 2,7-isomers

-4-

1 can be recovered by alternately hydrogenating and dehydrogenating the DMN
2 feed.

3

4 It has been disclosed that a noneutectic DMN mixture containing 2,6-DMN
5 and 2,7-DMN along with smaller amounts of other hydrocarbons can be
6 sublimated so that the remaining solid is a mixture of 2,6-DMN and 2,7-DMN.
7 However, no teaching is given that sublimation can be used to purify a
8 2,6-DMN/2,7-DMN mixture which is in the form of an eutectic composition.

9

10 Previous isomerization technologies have been limited to intra-triad
11 conversions, i.e., movement of methyl groups between adjacent alpha and
12 beta positions only. Santilli and Chen, U.S. Patent Application Serial
13 No. 08/892,508, filed July 14, 1997, which is incorporated herein by
14 reference, discloses a method of isomerizing a feed of any composition of
15 mixed dimethylnaphthalenes having a methyl group on each ring to a product
16 that approximates an equilibrium mixture of mixed dimethylnaphthalenes
17 having a methyl group on each ring (i.e., the 2,6-DMN and 2,7-DMN triads).
18 The method of the present invention incorporates this method of
19 isomerization across the two triads.

20

21 Researchers have integrated separation and isomerization technologies in an
22 attempt to improve the overall process of 2,6-DMN production. These various
23 attempts to integrate the technologies have had limited success because the
24 various steps of the process suffer from such problems as low yields or the
25 inability to isomerize between triads.

26

27 The technologies discussed above relate either generally or specifically to
28 certain aspects of the presently claimed invention. These technologies are
29 either not very effective or not economical for obtaining substantially pure
30 2,6-DMN from feeds containing a variety of DMN isomers outside the
31 2,6-triad. What is needed is an economic method to produce 2,6-DMN at

-5-

1 high purity and high yield from a mixture of DMN isomers without being limited
2 to the specific isomers present in the feed. A new method should convert
3 isomers other than 2,6-DMN into the desired 2,6-DMN isomer in order to have
4 an acceptable yield of 2,6-DMN from the feed source. The present invention
5 accomplishes these goals.

6 7 SUMMARY OF THE INVENTION

8
9 One object of the present invention is to provide an economical method of
10 separating 2,6-DMN from a mixture of DMN isomers in relatively high and
11 stable yields. The method is highly efficient in its use of dimethylnaphthalene
12 isomers, thereby enhancing the industrial significance of the process.

13
14 Another object of the present invention is to provide a method of purifying
15 2,6-DMN from a feed mixture of dimethylnaphthalene isomers and
16 near-boiling compounds comprising the steps of crystallizing the mixture to
17 precipitate a eutectic composition comprising 2,6-dimethylnaphthalene and
18 2,7-dimethylnaphthalene; optionally dissolving the eutectic composition in a
19 solvent; and recovering a predominantly 2,6-dimethylnaphthalene
20 composition from the dissolved eutectic composition by adsorbing out
21 non-2,6-dimethylnaphthalenes onto an adsorption column. The crystallization
22 accomplishes high recovery of 2,6-DMN independent of isomers present,
23 while the adsorption step accomplishes high purity of 2,6-DMN independent
24 of isomers present.

25
26 Still another object of the invention is to fractionate the feed mixture of
27 dimethylnaphthalene isomers and near-boiling compounds before it is purified
28 by crystallization and adsorption to remove compounds that are either more
29 volatile or less volatile than 2,6-DMN and 2,7-DMN. The fractionation step
30 simplifies downstream purification and reduces the size of downstream
31 equipment.

1
2 Yet another object of the invention is to recycle the DMN isomers,
3 predominantly isomers other than 2,6-DMN, that are either retained in the
4 mother liquor during the crystallization step or recovered in the extract stream
5 during the adsorption step to be isomerized into a mixture that closely
6 approximates an equilibrium distribution of dimethylnaphthalene isomers, that
7 can then be recycled back to the fractionation step.
8 Hydroisomerization/dehydrogenation is a highly efficient, nearly equilibrium
9 conversion of isomers other than 2,6-DMN into the desired 2,6-isomer.

10

11 BRIEF DESCRIPTION OF THE DRAWINGS

12

13 Figure 1 is a simplified process flow drawing of a preferred embodiment of the
14 invention.

15 Figure 2 is a graphical representation of the amounts of various DMN isomers
16 in an effluent over time.

17

18 Figure 3 is a graphical representation of a solvent crystallization experiment.

19 Figure 4 is a graphical representation of the amounts of 2,6-DMN versus
20 2,7-DMN in an effluent over time.

21

22 DETAILED DESCRIPTION OF THE INVENTION

23

24 A continuous process for the recovery and purification of 2,6-DMN from a
25 hydrocarbon feedstock containing mixed dimethylnaphthalene isomers has
26 been developed. The process of this invention is comprised of fractionation,
27 crystallization, adsorption, and isomerization steps. A simplified process flow
28 drawing of a preferred embodiment of this process is shown in Figure 1.

-7-

1 The feed for the new process is a hydrocarbon mixture that contains isomers
2 of dimethylnaphthalene (DMN). The concentration of DMNs in the feed is
3 preferably greater than 5 wt. %, more preferably greater than 50 wt. %, and
4 most preferably greater than 80 wt. %. Potential sources of hydrocarbon feed
5 are petroleum refinery streams, coal tar liquids, or the reaction products of a
6 synthetic chemical processing route. Examples of petroleum refinery streams
7 include, but are not limited to, higher boiling aromatic fractions produced in
8 reforming of petroleum naphtha to produce high octane gasoline; aromatic
9 fractions produced by the thermal cracking of catalytically reformed gasoline;
10 aromatic fractions produced by the catalytic cracking of thermally reformed
11 naphtha; aromatic concentrates obtained from catalytic gas oil produced in
12 catalytic cracking or petroleum; and crude unit gas oils. The mixed DMNs
13 could be produced from a chemical synthesis route such as , but not limited
14 to, dehydrocyclization of pentyltoluene made from the alkylation of pentenes
15 and toluene, dehydrocyclization of pentenyltoluene made from the
16 alkenylation of ortho-xylene and butadiene, or methylation of
17 methylnaphthalene. In a preferred embodiment, fresh feed is commingled
18 with recycle streams from the downstream isomerization step of this process.
19 Alternatively, the recycle can be introduced downstream of the fractionation
20 unit.

21
22 In a preferred embodiment, the feed is fractionated to obtain a heart cut that
23 is rich in DMN isomers and boils in the approximate range of 480-520°F,
24 preferably in the range 500-510°F. Fractionation can be accomplished by
25 conventional distillation in one or more distillation columns. If one column is
26 used, multiple feed and draw streams are required. The preferred
27 configuration is to use two columns. In the first column, components more
28 volatile than 2,6-DMN are distilled overhead and can be recovered as
29 valuable byproducts, recycled to earlier steps of the DMN production process,
30 or used as fuel. In the second column, components less volatile than
31 2,6-DMN are collected from the bottoms and can be recovered as valuable

1 by-products, recycled to earlier steps of the DMN production process, or used
2 as fuel. Fractionation may not be required prior to crystallization if the feed
3 has a sufficiently high concentration of DMN.

4
5 The fractionated DMNs can contain near-boiling components such as, but not
6 limited to, pentytoluenes, pentenyltoluenes, methylnaphthalenes,
7 ethylnaphthalenes, dimethylhydronaphthalenes, dimethyltetralins,
8 dimethyldecalins, trimethylindans, trimethylnaphthalenes as well as other
9 close-boiling aromatic, paraffinic, and naphthenic compounds. It is desirable
10 to minimize the concentration of components that would crystallize at a
11 temperature above the 2,6-DMN crystallization temperature in order to
12 minimize the simultaneous recovery of impurities with the desired 2,6-DMN
13 product.

14
15 In a preferred embodiment, the fractionated DMN mixture is cooled to
16 precipitate 2,6-DMN and a eutectic composition of 2,6-DMN and 2,7-DMN.
17 The final cooling temperature is dependent on the feed composition and
18 whether a solvent is added. For melt crystallization, the final cooling
19 temperature is as high as 230°F for a feed highly concentrated in 2,6-DMN, or
20 as low as 3°F for a feed dilute in 2,6-DMN. For the concentration range of
21 interest, the final cooling temperature is in the range of 155°F to 80°F. For
22 solvent crystallization, the final cooling temperature may vary over a wide
23 range depending on solvent and feed concentration but may range from
24 230°F to -120°F, preferably 80°F to 40°F. Pressure can be from 0 to
25 3000 psi. An alternative to cooling is to precipitate the 2,6-DMN and a
26 eutectic by a combination of cooling plus pressurizing the system to over
27 7000-20,000 psi. Crystallization may also be induced by removing solvent by
28 evaporation or by adding agents that reduce the solubility of DMN in solution.

29
30 The crystallization may be carried out batchwise or continuously. It may be
31 carried out in one vessel or more than one physically distinct vessel in series.

1 The preferred configuration depends on the relative concentrations of
2 2,6-DMN and other compounds that would co-precipitate, especially
3 2,7-DMN. If crystallization is carried out in one vessel, the maximum recovery
4 of 2,6-DMN is achieved by cooling the fractionated DMN mixture to the
5 2,6-DMN/2,7-DMN eutectic composition until all 2,6-DMN has precipitated. If
6 multiple crystallizers are used in series, 2,6-DMN is partially precipitated from
7 the mother liquor in the first crystallizer, separated from the supernatant, and
8 the supernatant is then transferred to one or more downstream vessels for
9 additional recovery of 2,6-DMN. Throughout the process, 2,6-DMN and the
10 2,6-DMN/2,7-DMN eutectic crystals are collected together. In the event that
11 isomers other than 2,6-DMN do not co-precipitate in one of the crystallizers
12 and there is a sufficiently high concentration of 2,6-DMN that is greater than
13 the eutectic composition, it may be advantageous to collect and recover
14 essentially pure 2,6-DMN prior to reaching the eutectic point.

15 The simplest crystallization technique is melt crystallization provided the
16 composition of 2,6-DMN plus 2,7-DMN in the feed mixture of DMNs is at least
17 20 wt. %, preferably at least 50 wt. %, and more preferably at least 90 wt. %.
18 Melt crystallization can be carried out in either a static or a dynamic design.
19 The mixture of DMN isomers is introduced into the crystallizer and the
20 contents are cooled with a non-contact heat transfer medium. The desired
21 crystals form on and adhere to the heat transfer surface. When essentially all
22 of the 2,6-DMN has solidified, the cooling is halted and the remaining liquid
23 contents are drained from the crystallizer. The heat transfer medium is then
24 heated slightly to melt the solids off of the heat transfer surface. The initial
25 melt will contain a higher concentration of impurities than the bulk of the
26 product so it can be collected separately and routed with the other DMN
27 isomers to the hydroisomerization/dehydrogenation unit in order to increase
28 the purity of the 2,6-DMN/2,7-DMN solution going to the adsorption step. The
29 mixture of liquid 2,6-DMN and 2,7-DMN are sent directly to the adsorption
30 step.

1 As an alternative, solvent crystallization can be used to separate the
2 2,6-DMN/2,7-DMN eutectic, and would be the preferred crystallization method
3 for feeds with low concentrations of 2,6-DMN plus 2,7-DMN. A solvent such
4 as a low boiling hydrocarbon like toluene, xylene, octane, or heptane, or an
5 alcohol like methanol, ethanol, or isopropanol, or other classes of solvents
6 such as ethers, or a low molecular weight carboxylic acid like acetic acid, or a
7 combination of solvents could be used. Light aromatic hydrocarbons are
8 preferred solvents with toluene and meta-xylene the most preferred.
9 Non-solvents may be added to enhance precipitation but these may impact
10 final product purity if they cannot be adequately separated in the adsorption
11 step. In a solvent crystallization process, the crystals of 2,6-DMN and
12 2,7-DMN are mechanically separated from the solution using, for example,
13 filters or centrifuges, and either melted or re-dissolved prior to being sent to
14 the adsorption step. The supernatant mixture will contain all DMN isomers,
15 including trace quantities of 2,6-DMN as well as near-boiling compounds, and
16 is sent to the hydroisomerization/dehydrogenation unit for further processing.
17
18 The crystals produced in a solvent crystallization process are optionally
19 washed with another agent such as methanol to remove mother liquor
20 retained between particles and contaminants that may adhere to the surface
21 of the particles. The crystals are once again mechanically separated from the
22 wash solution using, for example, filters or centrifuges. The washing agent is
23 cooled to near the crystallization temperature to minimize DMN dissolving into
24 the wash solvent. Following the wash, the crystals may optionally be dried
25 over mild heat to remove remaining wash agent and to partially sublime DMN
26 isomers other than 2,6-DMN. An acceptable alternative to solvent washing is
27 to partially melt the DMN crystals to remove the liquid impurities as is done in
28 a wash column.
29
30 The final purification step is adsorption separation of 2,7-DMN from 2,6-DMN.
31 The adsorption may be performed by either a simple swing-bed unit or, more

-11-

1 preferably, a simulated countercurrent moving bed unit. For a swing-bed unit,
2 one bed operates in adsorption mode while another operates in regeneration
3 mode. The adsorbent material selectively adsorbs 2,7-DMN from the feed
4 stream, leaving essentially pure 2,6-DMN in the effluent. When unacceptable
5 amounts of 2,7-DMN appear in the effluent, the operating bed is considered
6 to have reached the useful limit of its capacity to remove 2,7-DMN and it is
7 taken out of service. The other bed is placed on-line while the first bed is
8 regenerated and the cycle repeats itself. Multiple beds can be staggered in
9 adsorption mode and regeneration mode to optimize capital and operating
10 costs. Adsorption and regeneration can be carried out batchwise or
11 continuously. For a simulated countercurrent moving bed unit, the
12 2,6-DMN/2,7-DMN feed and a suitable desorbent are introduced to the
13 fixed-bed adsorption column at two different locations. Two product streams
14 are drawn from different locations along the column: an extract that contains
15 desorbent with 2,7-DMN and other impurities that were present in the feed,
16 and a raffinate that contains desorbent and essentially pure 2,6-DMN. The
17 DMNs are recovered from their respective adsorber effluent streams via
18 distillation. Desorbent is returned to the adsorber, 2,7-DMN is combined with
19 the supernatant from the crystallizer and routed to the
20 hydroisomerization/dehydrogenation unit, and 2,6-DMN is collected as
21 desired product.

22
23 Suitable adsorbents include crystalline aluminosilicates, L-zeolites, X-zeolites,
24 Y-zeolites, Y Offretite, and Amborsorb® 563 (a carbonaceous adsorbent).
25 The preferred adsorbents are Y-zeolites exchanged with Group I and/or
26 Group II metals (i.e., Na, K, Ca, Ba, etc.) with the most preferred Group I
27 metal being potassium. Suitable desorbents include, but are not limited to,
28 light aromatic hydrocarbons such as toluene, para-xylene, ethylbenzene, and
29 para-diethylbenzene. The preferred desorbents are aromatic hydrocarbons
30 and the most preferred is para-xylene. The desorbent may be a compound
31 with a higher boiling point than dimethylnaphthalene.

-12-

1
2 The preferred operating conditions for the adsorption process require
3 dissolution of the DMN feed mixture in a solvent. The DMN may be dissolved
4 to any concentration but the preferred concentration range is from 5% to 60%
5 DMN. The solvent may be any liquid that can dissolve DMN and at the same
6 time enhance adsorption selectivity. Suitable solvents are light aromatic
7 hydrocarbons, or aliphatic hydrocarbons with carbon number from 5 to 20,
8 with octane or heptane being the preferred solvents. Operating temperatures
9 can range from 80°F to 220°F, depending on concentration with a preferred
10 temperature of 140°F to 180°F. Operating pressure may vary but is set high
11 enough to maintain the solvent and DMN feed in a liquid state through the
12 column. The flow rate may vary but the preferred condition is with a liquid
13 hourly space velocity (LHSV) from 0.1 to 10 hr⁻¹.

14
15 The adsorbent should be carefully dried to the proper water content to
16 maximize the separation factor between 2,6-DMN and 2,7-DMN. Y-zeolite is a
17 low silica zeolite and, as such, it readily adsorbs moisture from air. If the water
18 content on the adsorbent is too high, the adsorbed water will reduce the
19 accessibility of the adsorbate molecules to the high surface area of the zeolite.
20 However, if the water content is too low, the adsorption selectivity of 2,6-DMN
21 and 2,7-DMN decreases.

22
23 Feed to the two-step hydroisomerization/dehydrogenation unit consists of
24 mixed DMNs depleted of 2,6-DMN as well as near-boiling components. In a
25 preferred embodiment, the source of these DMNs is the crystallizer
26 supernatant and adsorber extract as previously described. In addition, any
27 feed that is substantially depleted in 2,6-DMN, such as petroleum refinery
28 streams, coal tar liquids, or the reaction products of a synthetic chemical
29 processing route can be used exclusively or as co-feed with the supernatant
30 and extract.

31

-13-

1 Hydroisomerization/dehydrogenation is carried out as described in U.S.
2 Patent Application Serial No. 08/892,508 (Santilli and Chen), filed July 14,
3 1997, which is incorporated herein by reference. The aromatic rings of the
4 DMN molecules in the feed are first partially or completely saturated to form
5 dimethyltetralins (DMTs) and dimethyldecalins (DMDs) over a dual-functional
6 metal-acid catalyst (e.g., sulfided PdS/Boron-Beta with Al, sulfided
7 PtS/Boron-Beta with Al, sulfided PdS/Y-zeolite, or non-sulfided
8 Pd/Boron-Beta with Al). Methyl group migration readily occurs at reaction
9 conditions to produce a distribution of DMTs and DMDs with one methyl
10 group on each ring. The isomerized structures are converted back to an
11 essentially equilibrium distribution of DMNs by passing over a second catalyst
12 in a subsequent dehydrogenation reactor. The second catalyst is a reforming
13 catalyst that suppresses transalkylation, dealkylation, and cracking reactions
14 (e.g., sulfided Pt/Re/Al₂O₃, sulfided Pt/Na-ZSM-5, or PtS/Cs/Boron-SSZ-42).
15 In a preferred embodiment, the yield of partially saturated species (DMT) from
16 the hydroisomerization reaction should be at least 5 weight percent. In a
17 more preferred embodiment, the yield of partially saturated species (DMT)
18 should be at least 10 weight percent. The weight hourly space velocity
19 (WHSV) can vary from about 0.1 to 100 hr⁻¹, the pressure can vary from 0 to
20 3000 psi, the hydrogen/hydrocarbon molar ratio can vary from <0.1 to 100,
21 and the reactor temperature can vary from about 300°F to 1000°F.
22 Approximately 50% conversion of 2,7- to 2,6-triad dimethylnaphthalenes with
23 little or no formation of methylnaphthalenes, 1,2-DMN, 1,3-DMN, 1,4-DMN,
24 2,3-DMN or trimethylnaphthalenes can be achieved with this two-step process
25 through optimization of the process conditions. In all the embodiments of the
26 hydroisomerization/dehydrogenation process, the dimethylnaphthalene feed
27 can be flowed over the catalyst along with hydrogen gas or the reaction can
28 be performed batchwise.
29
30 DMN produced in the hydroisomerization/dehydrogenation unit is recycled
31 and recovered as product and DMN isomers other than 2,6-DMN are recycled

-14-

1 to extinction. In a preferred embodiment, the mixed-DMN product from the
2 hydroisomerization/dehydrogenation unit, hereinafter referred to as
3 isomerate, is recycled and combined with the hydrocarbon fresh feed to the
4 fractionation unit for removal of light and heavy contaminants. Alternatively,
5 contaminants in the isomerate could be removed in a separate and distinct
6 distillation unit and recovered as byproducts or fuel. For example, MN and
7 TMN could be transalkylated to produce DMN and increase the overall yield
8 of this process. In still another embodiment, in the absence of light or heavy
9 contaminants, the isomerate can be commingled with distilled DMNs from the
10 fractionation column as feed to the crystallization unit.

11

12 EXAMPLES

13

14 Example 1

15

16 The following example illustrates that a complex mixture of DMN isomers can
17 be separated by dissolving them in a solvent and passing the solution through
18 an adsorbent column. Furthermore, this example also illustrates that
19 2,6-DMN and 2,7-DMN isomers are well separated from each other in this
20 way. This example also illustrates that other isomers, such as 1,6-DMN,
21 1,5-DMN and 1,7-DMN, elute before 2,7-DMN and close to 2,6-DMN.
22 Therefore, using an adsorption purification process to recover 2,6-DMN when
23 the feed contains 1,6-DMN, 1,5-DMN and 1,7-DMN isomers, as in prior art,
24 has a reduced efficiency and therefor is more expensive to operate. The
25 adsorption process becomes much more efficient when a prior step is used to
26 remove or reduce the quantity of isomers other than 2,6-DMN and 2,7-DMN.

27

28 A mixture of DMN isomers having the composition 8.93% 1,7-DMN; 1.88%
29 1,5-DMN; 8.94% 1,6-DMN; 31.05% 2,7-DMN; and 49.20% 2,6-DMN was
30 dissolved in meta-xylene and passed through a column of potassium-
31 exchanged Y (K-Y) zeolite adsorbent. The weight of the adsorbent was

-15-

1 2.12 grams and the liquid hourly space velocity (LHSV) of the column was 1.2
2 hr^{-1} . At the interval between 40 and 50 minutes run time, the DMN in the
3 effluent was approximately 100% 2,6-DMN; and at 50 minutes run time the
4 proportion of concentration of effluent to concentration of feed, C_{eff}/C_o , was
5 approximately 0.2. At the interval between 50 and 60 minutes, the DMN in
6 the effluent was approximately 91.2% 2,6-DMN; and at 60 minutes run time,
7 the C_{eff}/C_o was approximately 0.75. At the interval between 60 and
8 70 minutes, the DMN in the effluent was approximately 81.5% 2,6-DMN; and
9 at 70 minutes run time, the C_{eff}/C_o was approximately 0.975. At the interval
10 between 70 and 80 minutes, the DMN in the effluent was approximately
11 74.5% 2,6-DMN, and at 80 minutes run time, the C_{eff}/C_o was approximately
12 1.05. A more complete graphical representation of the amounts of the
13 various DMN isomers in the effluent over time is shown in Figure 2.

14

15

Example 2

16

17 The following example illustrates the use of a coarse crystallization step to
18 reduce the level of non-2,6/2,7-isomers.

19

20 A mixture of isomers of 6.3 grams 1,6-DMN, 5.7 grams 1,7-DMN, 1.8 grams
21 1,5-DMN, 6.3 grams 2,7-DMN, and 6.3 grams 2,6-DMN was dissolved in
22 15 grams toluene, then cooled in a stirred vessel to 32°F. The solution was
23 filtered and a precipitate recovered. The precipitate was rinsed with cold
24 methanol, and then dried at ambient temperature under vacuum overnight.
25 The product was found to be 90% 2,6-DMN, 6% 2,7-DMN, and 3% other
26 DMN isomers.

27

28

Example 3

29

30 This example illustrates the overall separation process to produce pure
31 2,6-DMN from a feed of reformate oil.

-16-

1 Reformate oil from a chemical synthesis was purified to produce pure
2 2,6-DMN. The reformate had the composition shown below in Table A:

3
4 Table A

Component	Weight Percent
light components	0.06
toluene	1.8
C ₂ alkylbenzenes	0.60
C ₃ alkylbenzenes	1.88
C ₄ alkylbenzenes	2.61
indan	0.17
C ₅ alkylbenzenes	2.92
C ₂ indans	0.86
naphthalene	4.28
C ₆ alkylbenzenes	41.04
C ₃ indans	11.83
C ₃ indenenes	0.91
methylnaphthalenes	6.85
dimethylnaphthalenes	14.7
other	9.49

5
6 The first purification step was to distill a heart cut between 500°F and 520°F.
7 The resulting distillate composition is given below in Table B.
8
9 38 grams of distillate was diluted with 38 grams of toluene and cooled from
10 80°F to -5°F at a rate of 0.3°F/min in a stirred batch crystallizer. The relative
11 concentration of various DMN isomers in solution during this process is
12 shown in Figure 3. In Figure 2, it can be seen that the concentration of
13 2,6-DMN was reduced as temperature was reduced below 30°F. At
14 temperatures below 5°F, 2,7-DMN concentration also drops. However, the
15 other isomers present remained substantially in solution. These isomers

-17-

were therefore phase separated from the 2,6-DMN and 2,7-DMN. The solid precipitate formed was collected and separated from the adhering bulk fluid. The resulting precipitate composition is given below in Table B.

The precipitate was dissolved in m-xylene and fed to a column of adsorbent with K-Y zeolite. Effluent was recovered and dried. Product was essentially pure 2,6-DMN.

Table B

Compound	Distillate (wt%)	Precipitate (wt%)	Product (wt%)
1,7-dimethylnaphthalene	26.0	5.3	
1,3-dimethylnaphthalene	0.7	0	
1,5-dimethylnaphthalene	5.5	0	
1,6-dimethylnaphthalene	25.9	5.4	
2,7-dimethylnaphthalene	19.8	13.1	
2,6-dimethylnaphthalene	18.9	76.2	> 99.9
Other	3.2		

Example 4

This example illustrates the use of rough crystallization followed by adsorption where the feed has a high proportion of 2,6-DMN.

83.5 grams of a mixture of DMNs and meta-xylene (with the composition shown in Table C) was charged into a 250 ml glass-jacketed agitation vessel. A coolant was passed through the jacket to cool the solution from 75°F to 45°F at the rate of 1.8°F every 7 minutes. Solids precipitated and the resulting crystals were filtered through an 8 micron filter paper and recovered. The crystals were washed with a small amount of methanol and dried under vacuum. The purified crystals weighed 1.25 grams and the composition of

-18-

1 the solids analyzed is shown in Table C. The recovery of 2,6-DMN in this
2 crystallization example was calculated to be 16.4%.

3

4

Table C

Component	M-xylene	2,6-DMN	2,7-DMN	1,6-DMN	1,7-DMN	1,5-DMN
Feed: %	81.27	8.79	3.17	2.55	2.73	0.62
Crystal (solvent free)		98.85	1.15			

5

6 The recovered crystals were dissolved in meta-xylene to give a solution of
7 5% DMN. The above solution was pumped through a stainless steel column
8 (width 3/8"; length 12") packed with 5.7 grams of powdered K-Y zeolite. The
9 effluent concentration of DMN isomers was measured over time and is shown
10 in Figure 4. Solution was recovered for 105 minutes at which time 2,6-DMN
11 breakthrough was detected. The effluent recovered was dried and the
12 product was pure 2,6-DMN.

13

14

Example 5

15

16 This example illustrates the additional purification that can be obtained by a
17 partial sublimation process that occurs while drying.

18 A sample 2,6-DMN containing other DMN isomers was rinsed with cold
19 methanol. The methanol-wet mixture was analyzed and found to have the
20 composition reported, on a solvent-free basis, in Table D. The moist solid
21 was dried at room temperature overnight under vacuum. The resulting
22 composition is also reported in Table D.

23

Table D

	Wet Sample Composition (solvent-free basis)	Dried Sample Composition
2,6-DMN	52.3%	87.8%
2,7-DMN	13.6%	5.8%
1,6-DMN	11.1%	2.0%
1,5-DMN	6.1%	0.9%
1,7-DMN	13.9%	2.5%
other	3.0%	1.0%

Example 6

This example illustrates the additional purification that can be obtained by a partial sublimation process that occurs during a drying step.

A sample 2,6-DMN containing 2,7-DMN isomers was rinsed with cold acetone. The acetone-wet mixture was analyzed and found to have the composition reported, on a solvent-free basis, in Table E. The moist solid was dried at room temperature overnight under vacuum. The resulting composition is also reported in Table E.

Table E

	Wet Sample Composition (solvent-free basis)	Dried Sample Composition
2,6-DMN	91.7%	>99.9%
2,7-DMN	8.3%	<0.1

Although a few embodiments of the invention have been described in detail 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

-20-

1 of the invention. Accordingly, it is to be understood that all such modifications
2 and alterations are included within the spirit and scope of the invention as
3 defined by the following claims.

4

5 Footnote:

6 Ambersorb® is a registered trademark of Rohm & Haas Company.

-21-

1 WHAT IS CLAIMED IS:

2

3 1. A method of purifying 2,6-dimethylnaphthalene from a feed mixture of
4 dimethylnaphthalene isomers and near-boiling compounds comprising
5 the steps of:

6

7 (a) crystallizing the mixture to precipitate out of a supernatant a
8 precipitate comprising 2,6-dimethylnaphthalene and
9 2,7-dimethylnaphthalene;

10

11 (b) dissolving the precipitate in a solvent; and

12

13 (c) passing the dissolved precipitate through an adsorbent to recover
14 an effluent comprising 2,6-dimethylnaphthalene.

15

16 2. The method according to Claim 1, wherein the method further
17 comprises, before step (a), a fractionating step to remove compounds
18 more volatile and less volatile than 2,6-dimethylnaphthalene and
19 2,7-dimethylnaphthalene.

20

21 3. The method according to Claim 2, further comprising isomerizing
22 dimethylnaphthalene isomers other than 2,6-dimethylnaphthalene that
23 are retained in the supernatant from step (a) or adsorbed onto the
24 adsorbent from step (c) to convert the isomers to a mixture consisting
25 essentially of an equilibrium mixture of dimethylnaphthalene isomers.

26

27 4. The method according to Claim 3, wherein the equilibrium mixture of
28 dimethylnaphthalene isomers is recycled back to the fractionating step.

29 5. The method according to Claim 3, wherein the equilibrium mixture of
30 dimethylnaphthalene isomers is recycled back to the crystallizing step.

31

-22-

1 6. The method according to Claim 2, wherein, after step (c), the method
2 further comprises purifying the effluent by a method comprising:

3
4 (a) cooling the effluent to produce solid precipitate;

5
6 (b) washing the solid precipitate; and

7
8 (c) drying the washed precipitate under conditions permitting partial
9 sublimation of isomers other than 2,6-dimethylnaphthalene from
10 the precipitate.

11
12 7. The method of claim 1, wherein the feed mixture is prepared by a
13 process comprising the steps of:

14
15 (a) alkylation of toluene with a C₅ olefin or mixed C₅ olefins in the
16 presence of an alkali metal to form pentytoluenes; and

17
18 b) dehydrocyclization of the pentytoluenes over a catalyst comprising
19 a Group VIII metal or a mixture of Group VIII metals and a support
20 material.

21
22 8. The method of claim 7, wherein the Group VIII metal is selected from
23 the group consisting of Pt, Pd, Ni and Ir.

24
25 9. The method of claim 7, wherein the support material is alumina.

26 10. The method of claim 7, wherein the catalyst further comprises a metal
27 selected from the group consisting of Re, Ge and Sn.

28
29 11. The method of claim 1, wherein the feed mixture is prepared by a
30 method comprising the steps of:

31

-23-

- 1 (a) alkenylation of ortho-xylene with butadiene to form
2 pentenyltoluenes; and
3
- 4 (b) dehydrocyclization of the pentenyltoluenes in one or more steps to
5 form a mixture of dimethylnaphthalene isomers.
6
- 7 12. The method of claim 1, wherein the feed mixture is prepared by a
8 process comprising alkylating methylnaphthalene to form mixed
9 dimethylnaphthalenes.
10
- 11 13. The method of claim 1, wherein the feed mixture is prepared by a
12 process comprising fractionation of mixed hydrocarbon streams
13 resulting from petroleum refining.
14
- 15 14. The method of claim 1, wherein the feed mixture is prepared by a
16 process comprising fractionation of mixed hydrocarbon streams found in
17 coal tar liquids.
- 18 15. The method of claim 1, wherein, in step (a), the mixture is cooled.
19
- 20 16. The method of claim 1, wherein, in step (a), the mixture is cooled in a
21 solvent.
- 22 17. The method of claim 1, wherein, in step (a), the mixture is added to a
23 solvent and the solvent is evaporated.
24
- 25 18. The method of claim 1, wherein step (a) is carried out in one vessel.
26
- 27 19. The method of claim 1, wherein step (a) is carried out by partially
28 precipitating the 2,6-DMN and 2,7-DMN from the supernatant in a first
29 vessel and then by transferring the supernatant to a second vessel to
30 further precipitate 2,6-DMN and 2,7-DMN from the supernatant.

1

2 20. The method of claim 1, further comprising, before step (a), cooling the
3 feed mixture to just above 2,6-DMN/2,7-DMN's eutectic point and
4 recovering pure 2,6-DMN.

5

6 21. The method of claim 1, wherein step (c) uses two or more adsorption
7 vessels operating as a simulated counter-current moving bed unit.

8

9 22. The method of claim 1, wherein step (c) uses two or more adsorption
10 vessels operating as a swing-bed unit.

11

12 23. The method of claim 1, wherein the adsorbent comprises a material
13 selected from the group consisting of crystalline aluminosilicates,
14 L-zeolites, X-zeolites, Y-zeolites, Y Offretite, carbonaceous adsorbents
15 and mixtures thereof.

16

17 24. The method of claim 23, wherein the adsorbent is exchanged with
18 metals selected from the group consisting of Group I metals, Group II
19 metals and mixtures thereof.

20 25. The method of claim 24, wherein the adsorbent is exchanged with a
21 Group I metal.

22

23 26. The method of claim 25, wherein the adsorbent is exchanged with
24 potassium.

25

26 27. The method of claim 1, wherein the solvent in step (b) is a light aromatic
27 hydrocarbon.

28

29 28. The method of claim 1, wherein the solvent in step (b) is an aliphatic
30 hydrocarbon having a carbon number from 5 to 20.

31

- 1 29. The method of claim 28, wherein the solvent is heptane.
2
- 3 30. The method of claim 28, wherein the solvent is octane.
4
- 5 31. The method of claim 1, wherein the method further comprises
6 regenerating the adsorbent of step (c) with a desorbent comprised of an
7 organic solvent.
8
- 9 32. The method of claim 31, wherein the organic solvent is a light aromatic
10 hydrocarbon selected from the group consisting of toluene, xylenes,
11 ethylbenzene, and para-diethylbenzene.
12
- 13 33. The method of claim 32, wherein the organic solvent is para-xylene.
14
- 15 34. The method of claim 1, wherein the method further comprises, after
16 step (c), the steps of:
17
- 18 (a) hydroisomerizing over an acid catalyst the dimethylnaphthalene
19 isomers other than 2,6-dimethylnaphthalene that are retained in
20 the supernatant from step (a) or adsorbed onto the adsorbent in
21 step (c) to produce a mixture of dimethyldecalins and
22 dimethyltetralins; and
23
- 24 (b) dehydrogenating the mixture of dimethyldecalins and
25 dimethyltetralins.
26
- 27 35. The method of claim 1, wherein the steps are practiced in a continuous
28 manner.
29
- 30 36. The method of claim 1, wherein the steps are practiced in a batch
31 manner.