

METHOD OF MAKING DIMETHYLNAPHTHALENES

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority from U.S. Provisional Application Serial No. 60/078,222, filed March 16, 1998.

I. FIELD OF THE INVENTION

The invention relates to a method of making dimethylnaphthalenes.

II. BACKGROUND OF THE INVENTION

Dimethylnaphthalenes ("DMN") are valuable for use in a variety of chemical manufacturing processes. 2,6-dimethylnaphthalene ("2,6-DMN"), e.g., is particularly valuable. 2,6-DMN is a precursor for 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 which provides superior strength and heat resistance compared to polyethylene terephthalate ("PET") in applications such as films (e.g., photographic film), fibers, containers and molded parts and has, therefore, unique commercial advantages. Thus, there has been recently worldwide increasing interest in the production of 2,6-DMN, 2,6-NDA and 2,6-NDC.

Naturally, there is an interest in having an economical and efficient process for their manufacture. 2,6-NDA and 2,6-NDC production is similar to that of terephthalic acid in that a 2,6-dialkylnaphthalene, e.g., 2,6-DMN, is oxidized to the corresponding acid by using well established methods. Thus, the challenge lies in the manufacture of dialkylnaphthalenes (especially DMN's) from which the 2,6-dialkylnaphthalenes are produced then via a variety of

1 methods including isomerization and separations. As a result, it is highly
2 desirable to find an economical way to manufacture DMN's, particularly
3 2,6-dialkylnaphthalenes, and especially 2,6-DMN.

4 Several conventional methods for producing 2,6-naphthalene dicarboxylic
5 acid precursors are known. These methods, which all lead to production of
6 DMN's, can be grouped as follows:

7 (1) alkenylation/cyclization/dehydrogenation, starting with a monocyclic
8 aromatic and a diolefin, (2) reforming/recovery from kerosene fractions,
9 (3) recovery from cycle oil produced in fluid catalytic cracking (FCC)
10 operations, and (4) transalkylation of naphthalene with polyalkylbenzenes. In
11 addition, alkylation (e.g., methylation or propylation) of naphthalene is also an
12 alternative method to produce dialkylnaphthalenes.

13 In regards to the first category of methods listed above, U.S. Patent
14 No. 4,990,717 discloses a method for production of a monoalkenylated
15 aromatic via base-catalyzed reactions. The reactions are performed by
16 reacting an alkylbenzene (e.g., ortho-xylene or para-xylene) with a C₄ or C₅
17 conjugated diene over a fixed bed of supported alkali metal catalyst. Similar
18 reactions using a dispersed alkali metal catalyst are also disclosed in a
19 number of even earlier patents such as U.S. Patent Nos. 3,953,535,
20 3,954,895 and 3,954,896. Another known process teaches a method for
21 producing pentyltoluenes. This method is disclosed in U.S. Patent
22 No. 3,931,348 (the '348 patent). The '348 patent teaches producing DMN's
23 from a pentyltoluene/pentenyltoluene obtained from addition of p-xylene and
24 butene or butadiene.

25 These various approaches are each aimed at making
26 pentyltoluenes/pentenyltoluenes which can be then selectively converted.
27 The conversion is via a subsequent cyclization and dehydrogenation step to
28 DMN's which belong to the same DMN triad as 2,6-DMN (*vide infra* for the
29 DMN triads). Discovery of an alternative method to these known methods for

1 making DMN's is highly desirable. These known methods are expensive
2 because they involve the relatively expensive starting materials, the relatively
3 expensive base catalysts and the restrictions on manufacturing those DMN
4 precursors which can be selectively converted to the DMN's belonging to the
5 2,6-DMN triad.

6 Other methods for the two-stage process of cyclization and dehydrogenation
7 reactions are disclosed, for example, in U.S. Patent Nos. 5,012,024,
8 5,030,781, 5,073,670 and 5,118,892. In those references, cyclization of
9 monoalkenylated toluene is accomplished over a zeolite catalyst containing
10 platinum and copper to a dimethyltetralin such as 1,5-dimethyltetralin. These
11 references teach that dehydrogenation of dimethyltetralins typically takes
12 place over a platinum/rhenium catalyst supported on alumina. This method is
13 also undesirable since it involves at least two distinct steps and is relatively
14 expensive.

15 Yet another known process teaches alkylating toluene with 1-pentene. This
16 method is taught in U.S. Patent No. 5,043,501. The resulting alkylate is then
17 catalytically dehydrocyclized by contacting with a zeolite L to produce DMN's.
18 This process, however, has many drawbacks. Pure 1-pentene streams are
19 unduly expensive and the yield of DMN's with zeolite L is very poor.

20 A combined cyclization and dehydrogenation operation is taught in U.S.
21 Patent No. 5,068,480. The process comprises subjecting 2-methyl-1-(p-tolyl)-
22 butene, 2-methyl-1-(p-tolyl)-butane or a mixture thereof to cyclization and
23 dehydrogenation in the presence of a catalyst comprising lead oxide and/or
24 indium oxide and aluminum oxide. However, similar to the known methods
25 described before, this method intends to make DMN's which belong to the
26 same DMN triad as 2,6-DMN.

27 As regards the second method stated above for making DMN's, several
28 patents (e.g., U.S. Patent No. 4,963,248; Japanese Patent Nos. 02,247,136,

1 02,247,137, 02,304,034 and 03,038,532) describe the reforming of
2 hydrotreated kerosene fractions and recovery of DMN's from the reformat.
3 These references claim improved results are obtained by first removing the
4 normal paraffins from the kerosene fraction using molecular sieve
5 separations. Reforming is typically done over a platinum on alumina catalyst
6 at 750-1020°F and about 350 psig in the presence of hydrogen to obtain a
7 reformat containing about 18 percent DMN's. 2,6-DMN can be separated
8 from the reformat via distillation, molecular sieve adsorption, crystallization
9 or complexation. This method does not meet the current requirements for
10 economy since the process results in a low DMN yield and even lower
11 2,6-DMN yield. In addition, the resulting DMN mixture usually consists of all
12 10 DMN isomers, which is typical of the DMN products directly manufactured
13 from refinery streams and results in inefficiency in the subsequent steps of
14 producing 2,6-DMN via isomerization and separations.

15 As regards the third method stated above for making DMN's, several
16 references teach recovery of 2,6-DMN from FCC Light Cycle Oil (proposed in
17 a study by Eldib Engineering Co., see *Chemical Week*, 6/24/1992, p. 27;
18 *European Chemical News*, 9/28/1992, p. 30; *Chemical Marketing Reporter*,
19 10/12/1992; *Chemical Week*, 11/4/1992, p. 39). As disclosed, the material,
20 which is ordinarily used as a diesel fuel blendstock, contains about 1.75%
21 2,6-DMN. It is disadvantageously accompanied by all other 9 DMN isomers
22 as in the case of kerosene described above. A key problem with this
23 approach is that the FCC Cycle Oil contains high concentrations of sulfur and
24 nitrogen compounds. These contaminants poison zeolites used in recovery of
25 2,6-DMN and also isomerization catalysts. To remove the sulfur and nitrogen
26 compounds and to reduce them to about 10 ppm each, hydrotreating at
27 severe conditions is required. Hydrotreating under such severe conditions
28 inevitably causes hydrogenation and hydrocracking of DMN's, resulting in a
29 great reduction in the yield of DMN's.

1 As regards the fourth method stated above for making DMN's, several patents
2 teach methods of manufacturing DMN's by transalkylation of naphthalene or
3 2-methylnaphthalene. These patents are, for example, U.K. Patent
4 No. 2,246,788A and European Patent No. 0,494,315 A1. However, it is
5 apparent that such methods are always associated with by-products such as
6 trialkylnaphthalenes and have a low efficiency. These by-products are
7 undesirable due to reduced yield of the desired products and added
8 complexity and cost to the process because of the need for further separation
9 steps. Similar drawbacks are also unavoidable with the methods of making
10 DMN's by alkylation of naphthalene or methylnaphthalenes.

11 Accordingly, there exists a need in the petroleum industry for a lower-cost
12 method than presently exists of producing DMN's. The method of this
13 invention provides such a method.

14 III. SUMMARY OF THE INVENTION

15 The method of the invention utilizes amorphous catalysts in the reforming step
16 which are superior in performance to those catalysts previously taught for use
17 in making DMN's. Due to the recent efforts to increase oxygenate content of
18 fuels, tertiary-amyl-methyl ether ("TAME") units are in operation in many
19 petroleum refineries. The raffinate streams of TAME units contain C₅ olefins.
20 In addition, an FCC C₅ stream also comprises C₅ olefins. In some
21 embodiments of the invention, this raffinate and/or FCC C₅ stream are
22 advantageously as a relatively low-cost feed stream for the production of
23 pentyltoluenes, which then are used in making DMN's. The invention in some
24 embodiments includes the discovery of performance enhancing properties of
25 having a co-feed/diluent in the reforming step.

26 In one embodiment, the invention includes a method of making DMN's,
27 including contacting in a reforming zone a pentyltoluenes containing feed with
28 a platinum-containing amorphous reforming catalyst, containing a metal
29 selected from the group consisting of a non-platinum Group VIII B metal,

1 rhenium, germanium, tin, lead, gallium, indium, and mixtures thereof, at
2 reforming conditions, where at least a portion of the pentyltoluenes is
3 converted to DMN's.

4 In another embodiment, the invention includes a method of making DMN's,
5 the method including passing a C₆–C₁₂ naphtha-containing stream and a
6 pentyltoluenes-containing stream to a reforming zone containing an
7 amorphous platinum/alumina reforming catalyst; contacting in the reforming
8 zone, the C₆–C₁₂ naphtha-containing stream and the pentyltoluenes and the
9 reforming catalyst, under reforming conditions, where: at least a portion of the
10 pentyltoluenes is converted to DMN's; and at least a portion of the C₆–C₁₂
11 naphtha is converted to aromatics.

12 In another embodiment, the invention includes a method of making DMN's,
13 the method including passing a diluent stream, selected from benzene,
14 toluene, xylenes, or C₅ naphtha, and a pentyltoluenes-containing stream to a
15 reforming zone containing an amorphous platinum/alumina reforming catalyst;
16 contacting in the reforming zone, the diluent stream and the pentyltoluenes
17 and the reforming catalyst, under reforming conditions, where at least a
18 portion of the pentyltoluenes is converted to DMN's.

19 In yet another embodiment, the invention includes a method of making
20 DMN's, the method including: contacting in an alkylation zone, at a
21 temperature of from about 32°F to about 500°F and a pressure of from about
22 ambient to about 500 psig, a toluene-containing stream with a pentene-
23 containing TAME raffinate stream in the presence of an acid alkylation
24 catalyst selected from the group consisting of aluminum chloride, acid clays,
25 heteropolyacids, acidic zeolites having a pore diameter of at least about
26 4.5 angstroms, solid-phosphoric acid catalysts, and mixtures thereof, where at
27 least a portion of the toluene and pentene-containing TAME raffinate react to
28 form pentyltoluenes; recovering from the alkylation zone at least a portion of
29 the pentyltoluenes; passing a C₇ naphtha-containing stream and at least a

1 portion of the pentyltoluenes to a reforming zone containing an amorphous
2 platinum/alumina reforming catalyst including a metal selected from the group
3 consisting of a non-platinum Group VIII B metal, rhenium, germanium, tin,
4 lead, gallium, indium, and mixtures thereof; contacting in the reforming zone,
5 the C₇ naphtha-containing stream and the pentyltoluenes and the reforming
6 catalyst, under reforming conditions including a pressure from about ambient
7 to about 500 psig and a temperature from about 700°F to about 1000°F,
8 where: at least a portion of the pentyltoluenes is converted to DMN's; and at
9 least a portion of the C₇ naphtha is converted to toluene; and recovering from
10 the reforming zone at least a portion of the DMN's; passing at least a portion
11 of the toluene produced in the reforming zone to the alkylation zone.

12 IV. BRIEF DESCRIPTION OF THE DRAWING

13 Figure 1 depicts, in one embodiment, a simplified schematic process flow
14 diagram of the method of the invention.

15 Figure 2A is the same as Figure 1, except that it does not show a
16 dehydrogenation unit between the alkylation zone and reforming zone and
17 does show a TAME unit as the source of the pentene-containing feed stream.

18 Figure 2B is the same as Figure 2A, except that it shows a dehydrogenation
19 unit between the alkylation zone and reforming zone.

20 Figure 3 is the same as Figure 1, except that it shows a separation zone
21 following the reforming zone, shows a co-feed/diluent stream to the reforming
22 zone, and shows a recycle stream from the separation zone to the alkylation
23 zone.

24 Figure 4 is the same as Figure 1, except that it shows a co-feed/diluent
25 stream to the reforming zone.

1 V. DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

2 A. Steps of the Process

3

4 In one embodiment, the method of the invention includes contacting an
5 alkylated toluene with a reforming catalyst, at reforming conditions, wherein at
6 least a portion of the alkylated toluene is converted to DMN's. The alkylated
7 toluene is alkylated with an alkyl group which includes, but is not limited to, a
8 pentyl or pentenyl group.

9

10 In another embodiment, the alkylated toluene is the product of contacting, in
11 an alkylation unit, at alkylation conditions, in the presence of an alkylation
12 catalyst, toluene with a pentene-containing stream. The pentene-containing
13 stream is optionally a TAME unit raffinate, a mixture of pentenes obtained
14 from selective dehydrogenation of pentanes, purchased 1-pentene, an FCC
15 C₅ stream (with or without having any iso-amylene removed), a C₅ olefin
16 containing stream from an ethylene or naphtha cracker, a resid coking unit, an
17 olefin metathesis unit, an olefin oligomerization unit producing C₅ olefins as a
18 side product, a C₅ olefin-containing stream from alcohol dehydration. The
19 olefin streams, or both the olefin and aromatic streams, are optionally fed by
20 staged addition.

21

22 When the pentene-containing stream is from a TAME raffinate, the TAME
23 raffinate stream is any conventional TAME raffinate stream containing
24 pentenes. Optionally, a separate conventional adsorbent step may be used
25 for removal of iso-amylene. The conversion of pentyltoluenes to
26 pentenyltoluene is a process option discussed later in this description.

27

28 The toluene-containing stream is optionally pure, i.e., not obtained from a
29 refinery stream, although various concentrations are possible. Alternatively,
30 the toluene-containing stream is obtained from any conventional refinery
31 stream containing toluene. These two streams are both fed to an alkylation

1 zone. The streams are optionally mixed either prior to or after entering the
2 alkylation zone. The alkylation zone utilizes any conventional alkylation
3 process. The units in the alkylation process will typically include a reactor and
4 one or more distillation columns for fractionating the alkylation reactor
5 product. In another embodiment of the invention, the pentyltoluenes are
6 prepared via alkylation steps other than toluene alkylation with C₅ olefins. For
7 example, pentyltoluenes and/or pentenyltoluenes are optionally prepared via
8 base-catalyzed alkylation of xylene(s) with C₄ olefins and/or C₄ dienes.

9
10 In the embodiment utilizing toluene and a C₅ olefin containing stream, at least
11 a portion of the pentenes and toluene are converted in the alkylation unit to
12 pentyltoluenes. Such process should include an acid alkylation catalyst.
13 Such catalyst is optionally selected from the group consisting of aluminum
14 chloride, acid clays, solid phosphoric acid catalysts, heteropolyacids, acidic
15 zeolites having a pore diameter of at least about 4.5 angstroms, and mixtures
16 thereof. Acidic zeolites having a pore diameter of at least about
17 4.5 angstroms include, but are not limited to, the following zeolites: Y zeolite,
18 beta zeolite, mordenite, offretite, omega, ferrierite, SSZ-20, SSZ-24, SSZ-25,
19 SSZ-26, SSZ-31, SSZ-32, SSZ-33, SSZ-35, SSZ-37, SSZ-42, SSZ-44, EU-1,
20 NU-86, NU-87, UTD-1, ZSM-5, ZSM-11, ZSM-12, ZSM-35, ZSM-48, MCM-22,
21 MCM-36, MCM-56, and mixtures thereof. In one embodiment, the acid
22 alkylation catalyst is preferably a Y-zeolite type catalyst. The alkylation
23 catalyst optionally includes up to 80 weight percent alumina as binder,
24 preferably up to 50 weight percent alumina.

25
26 To prevent the formation of tri-substituted benzene compounds during the
27 alkylation of toluene to pentyltoluenes, it is favorable to have toluene in
28 stoichiometric abundance. Unreacted toluene is generally separated from the
29 pentyltoluenes before the pentyltoluenes are dehydrocyclized. Based on the
30 results demonstrated in Example 19 below, the separation of toluene from
31 pentyltoluenes after the alkylation step may not be required before the
32 reforming step of pentyltoluenes to DMN's.

1 In addition, the separation of the C₅ alkanes/naphthenes, which are inert for
2 toluene alkylation and may be present in the C₅ olefin stream, from C₅ olefins
3 before or after toluene/C₅ olefin alkylation step may not be required. These
4 C₅ alkanes/naphthenes may be used as diluent for the reforming of
5 pentyltoluenes to DMN's as well. One or more conventional separation units
6 may be used to separate out unreacted pentenes and toluene. Optionally,
7 distillation units are utilized to further purify the pentyltoluenes. Optionally,
8 some or all of any dipentyltoluenes by-product formed in the alkylation zone is
9 removed from the alkylation zone product. At least a portion of the
10 pentyltoluenes stream recovered from the alkylation zone, and optionally any
11 unseparated dipentyltoluenes, are then passed to a reforming zone to make
12 DMN's. It is optionally passed as-is or with a diluent or a co-feed. The diluent
13 is an inert-acting solvent, e.g., excess toluene, benzene, xylenes, C₅ naphtha,
14 or mixtures thereof. Suitable co-feeds are C₆–C₁₂ naphthas. These co-feeds
15 optionally serve both as diluents and as reactants. They typically reform to
16 aromatics. Where C₇ naphtha is used as a co-feed, a portion of the C₇
17 naphtha is typically converted to toluene in the reforming zone. That toluene
18 is then optionally separated from the other reformer effluents for recycle to the
19 alkylation unit to make pentyltoluenes. In the reformer unit, the weight ratio of
20 co-feed or diluent to pentyltoluenes containing feed is from about 0:1 to about
21 1000:1, preferably from about 1:1 to about 100:1.

22 The reforming zone utilizes any conventional reforming reactor bed
23 arrangement. The reforming zone contains a reforming catalyst, e.g., a
24 dehydroaromatizing catalyst. This catalyst is preferably one with high DMN
25 selectivity and low hydrocracking selectivity. Suitable catalysts are platinum-
26 containing amorphous reforming catalysts which optionally contain a metal
27 selected from the group consisting of a non-platinum Group VIII B metal,
28 rhenium, germanium, tin, lead, gallium, indium, and mixtures thereof. Any
29 conventional impregnation, mulling, ion exchange or other known methods for
30 adding the metals may be used. The support of the amorphous catalysts is
31 optionally selected from the group consisting of alumina, silica, titania,

1 vanadia, chromia, zirconia, and mixtures thereof. Preparations of such
2 catalysts are taught, e.g., in U.S. Pat. Nos. 3,415,737; 4,636,298; and
3 4,645,586, the disclosures of which are incorporated herein by references. In
4 one preferred embodiment, the reforming catalyst is preferably a non-zeolitic
5 platinum-rhenium catalyst supported on alumina. Commercial examples of
6 such catalysts are, for example, (1) AR405, CR201/301/401, E1000, E301,
7 E302, E603, E611, E802, E803, RG492 and RG582 from ACREON
8 CATALYSTS/PROCATALYSE; (2) CK-300's, CK-433, CK-522 Trilobe,
9 KC-542 Trilobe, ARC-555, ARC-111E and ARC-111B from AKZO NOBEL;
10 (3) PHF-5, PRHF-30/33/37/50/58, KX-120/130/160, PHF-4, P-8, PR-8, PR-9,
11 PR-28, PR-29, IMP-RNA-2/4, PS-7, PS-10, PS-20, PS-30 and PS-40 from
12 CRITERION CATALYST CO. LP; (4) R-30, R-32, R-34, R-50, R-51, R-56,
13 R-60, R-62, R-132, R-134 and R-72 from UOP (see the "OGJ Special
14 *Worldwide Catalyst Report*" in *Oil & Gas Journal*, October 6, 1997, p. 43); and
15 (5) Rhen-F and Rhen-H from Chevron.

16

17 In the reforming stage, the pentyl group is dehydrogenated and cyclized
18 intramolecularly to produce DMN's. Preferably, the formation of
19 ethylnaphthalenes ("EN") is low or negligible. This is because their boiling
20 points are very close to those of DMN's and, therefore, they are difficult to
21 separate out. Optionally, one or more separation units are used to recover
22 the DMN's, especially 2,6-DMN. As a result of the reforming, at least a
23 portion of the pentyltoluenes is converted to DMN's. The preferable form is
24 2,6-DMN. The effluent from the reforming zone is passed to a separation
25 zone for recovery of at least a portion of the DMN product. Any conventional
26 separation methods are optionally utilized. Optionally, the DMN's are further
27 purified and isomerized to increase yield of 2,6-DMN. Where only partial
28 conversion of pentyltoluenes to DMN's is achieved, the process optionally
29 includes a separation stage for recovering at least a portion of the
30 pentyltoluenes not converted to DMN's. At least a portion of any unconverted
31 pentyltoluenes is then, optionally, recycled to the reforming unit.

32

1 The reformer unit utilized in the present invention is optionally either a
2 dedicated unit or a multipurpose unit. That is, in one embodiment, the
3 reformer unit is dedicated to the production of DMN's. In another
4 embodiment, the reformer unit has feed streams other than for the production
5 of DMN's and makes products other than DMN's. For example, reformers are
6 also utilized in the production of gasoline range aromatics and for making
7 benzene. This latter embodiment is economically beneficial since there are
8 no capital costs of constructing a dedicated reformer unit. That is, a relatively
9 small stream of pentytoluenes is co-fed into the naphtha feed stream of an
10 existing reformer. Naturally, a separation step follows the reformer to
11 separate the DMN's from any other reformer products.

12 Steps of treating the reformer effluent for increasing the yield of and/or
13 purifying the preferred 2,6-DMN optionally follow the reformer unit. One such
14 optional step is isomerization of the reformer effluent to increase the yield of
15 2,6-DMN. Santilli and Chen, U.S. Patent Application Serial No. 08/892,508
16 ("the '508 Application"), which is incorporated herein by reference, discloses a
17 method of isomerizing a feed of any composition of mixed DMN's having a
18 methyl group on each ring to a product that approximates an equilibrium
19 mixture of mixed DMN's having a methyl group on each ring (i.e., the
20 2,6-DMN and 2,7-DMN triads). A method utilizing crystallization and
21 adsorption for purifying the 2,6-DMN from the reformer effluent is taught by
22 Munson, Bigot, and He, U.S. Patent Application Serial No. 09/000,858, which
23 is incorporated herein by reference. One or more embodiments of the method
24 of the present invention optionally incorporate these methods, separately
25 and/or in combination. These methods of purification and isomerization
26 enhance the value of the present invention for making a mixture of DMN's
27 which belong to the 2,6-DMN and 2,7-DMN triads. That is, where 2,6-DMN is
28 the desired end product, being able to produce a mixture of DMN's is valuable
29 in itself where methods exist for then isomerizing/purifying that mixture into
30 2,6-DMN. This provides an economic benefit where the feed streams for
31 producing a mixture of DMN's through alkylation and reforming are less

1 expensive than the feed streams necessary for producing mainly 2,6-DMN
2 through alkylation and reforming.

3

4 The isomerization method taught in the '508 Application solves a long felt
5 need to overcome a fundamental complication in the commercial production
6 of 2,6-DMN. That fundamental complication is the difficulty of converting
7 DMN isomers other than 2,6-triad DMN's into the desired 2,6-DMN isomer.
8 There are ten different isomers of DMN's. Of these, nine of them can be
9 grouped into three triads based on the relative ease of acid-catalyzed
10 isomerization within a certain triad. Such an intra-triad isomerization can be
11 done using a wide variety of solid acids as catalysts. This ease of acid-
12 catalyzed isomerization within a triad is based on the fact that a methyl group
13 on naphthalene shifts relatively easily from an alpha position to a beta position
14 or vice versa on the same ring but does not shift easily from a beta position to
15 another beta position on the same ring or from an alpha position to another
16 alpha position. The three triad groups are as follows: 2,7-DMN, 1,7-DMN and
17 1,8-DMN; 2,6-DMN, 1,6-DMN and 1,5-DMN; and 1,4-DMN, 1,3-DMN and
18 2,3-DMN. The tenth isomer, 1,2-DMN, consists of two methyl groups in
19 adjacent alpha and beta positions and does not fall into one of the
20 aforementioned triads.

21

22 In conventional methods, DMN manufacturers have focused on developing
23 the methods (*vide supra*) for making commercial quantities of 2,6-DMN by
24 avoiding co-producing other DMN isomers because of the difficulty in
25 recovering 2,6-DMN at high yield in the presence of other DMN isomers.
26 Based on the above described DMN triad chemistry, DMN manufacturers
27 have tried to avoid making isomers outside the 2,6-triad because of the
28 difficulty in isomerizing across triads and the associated unavoidable side-
29 reactions such as cracking, dealkylation and transalkylation. Isomers that
30 cannot be converted to 2,6-DMN represent a yield loss and inefficient use of
31 raw materials. Adsorption separation and purification of the 2,6-DMN are not
32 practical when the concentration of 2,6-DMN in the feed stream is low. This is

1 because there are no known materials that will preferentially adsorb 2,6-DMN
2 over the other isomers. These limitations often necessitate the use of
3 expensive raw materials and controlled organic synthesis reactions that can
4 produce only isomers in the 2,6-triad, such as alkylation of butadiene and
5 ortho-xylene.

6
7 Thus, previous isomerization technologies have been limited to intra-triad
8 conversions, where the technologies of manufacturing 2,6-DMN are,
9 therefore, preferably those which mainly make 2,6-triad DMN's. Briefly, the
10 new method taught in the '508 Application consists of hydroisomerization of
11 DMN's over a bifunctional catalyst (metal and acid) and subsequent
12 dehydrogenation of the resulting partially and/or fully saturated DMN's. Thus,
13 this new method opens up a new opportunity of more efficiently making
14 2,6-DMN from not only 2,6-triad but also 2,7-triad. Again, this new
15 isomerization enhances the value of the instant method since it lifts the
16 limitation on making 2,6-DMN from the precursors which mainly make
17 2,6-triad DMN isomers.

18
19 **B. Process Conditions**

20
21 The alkylation zone, reforming zone, and any separation zones are each
22 operated under conventional operating conditions, e.g., pressure,
23 temperature, and flow rates. Such conditions are known in the art. Typical
24 alkylation conditions, e.g., include a temperature from about 32°F to about
25 500°F, a pressure from about ambient to about 500 psig, preferably from
26 about ambient to about 300 psig for a Y-zeolite, and preferably from about
27 32°F to about 300°F for AlCl_3 and from about 100°F to about 400°F for a
28 Y-zeolite. In one embodiment, a preferred toluene to pentenes molar ratio is
29 from about 4:1 to about 12:1 and the Weight Hourly Space Velocity ("WHSV")
30 of the feed is from about 1 h^{-1} to about 8 h^{-1} .

31

1 Conventional residence times are used as appropriate for each particular
2 catalyst. An acid zeolitic alkylation catalyst such as Y-zeolite is preferred
3 since it can be regenerated and reused. In contrast, AlCl_3 cannot be reused.
4 Typical alkylation zone conditions and catalysts are taught, e.g., in U.S.
5 Patent No. 5,149,894, the disclosure of which is incorporated herein by
6 reference.

7
8 Typical reforming conditions, e.g., are a temperature from about 700°F to
9 about 1000°F, a pressure from about ambient to about 500 psig. In one
10 preferred embodiment, the pressure is from about ambient to about 300 psig,
11 the temperature is from about 800°F to about 1000°F, and the catalyst is a
12 Pt-Re/ Al_2O_3 /Cl amorphous reforming catalyst. The Weight Hourly Space
13 Velocity (WHSV) of pentyltoluenes is typically from about 0.01 to about
14 100 h^{-1} , in some embodiments preferably from about 0.1 h^{-1} to about 10 h^{-1} ,
15 more preferably from about 0.1 h^{-1} to about 1 h^{-1} . The molar ratio of hydrogen
16 to hydrocarbon feed is typically from about 1:1 to about 15:1. In some
17 embodiments, the ratio is preferably from about 1:1 to about 6:1.

18 Conventional residence times are used as appropriate for each particular
19 catalyst. Typical reforming conditions are taught, e.g., in U.S. Patent
20 Nos. 5,401,386, 5,328,595, and 4,645,586, the disclosures of which are
21 incorporated herein by references.

22
23 Optionally, prior to passing the pentyltoluenes to the reforming zone, at least a
24 portion of the pentyltoluenes is converted to pentenyltoluenes. This is
25 accomplished by contacting at least a portion of the pentyltoluenes with a
26 conventional dehydrogenation catalyst at conventional dehydrogenation
27 conditions. As a result, at least a portion of the pentyltoluenes is
28 dehydrogenated to form pentenyltoluenes.

29
30 Thus, a mixture of pentyltoluenes and pentenyltoluenes is formed. Preferably,
31 the mixture contains from about 10 weight percent to about 90 weight percent

1 pentenyltoluenes. More preferably, the mixture contains from about 25 weight
2 percent to about 65 weight percent pentenyltoluenes. At least a portion of this
3 mixture is passed to the reforming zone for contact with the reforming catalyst
4 as described above. Optionally, pentenyltoluenes are produced via toluene
5 alkenylation with pentadienes on acid catalysts. The production of
6 pentenyltoluenes via toluene alkenylation with pentadienes is optionally
7 accomplished together with the production of pentytoluenes via toluene
8 alkylation with pentenes in the same process step.

9 VI. DETAILED DESCRIPTION OF THE DRAWINGS

10

11 Modifications of the process that is shown in the drawings and described in
12 this specification that are obvious to those of ordinary skill in the oil refinery
13 process art are intended to be within the scope of the invention.

14

15 One embodiment of the process of the invention is illustrated in the Figure 2B.
16 A toluene-containing stream 15 is contacted with a pentene-containing TAME
17 raffinate stream 10 obtained from TAME unit 5. The contacting occurs in
18 alkylation zone 20 in the presence of an acid alkylation catalyst (not shown).
19 At least a portion of the toluene and pentenes react to form pentytoluenes.
20 Pentytoluenes are recovered in stream 25.

21

22 At least a portion of pentytoluenes stream 25 is passed to a reforming
23 zone 30. The reforming zone 30 contains a dehydroaromatizing type catalyst
24 (not shown). In reforming zone 30, the pentytoluenes in stream 25 are
25 contacted with a dehydroaromatizing type catalyst (not shown) under
26 reforming conditions. At least a portion of the pentytoluenes is converted to
27 DMN's, preferably 2,6-DMN. At least a portion of the DMN's is recovered as
28 stream 35.

29

30 Optionally, prior to passing stream 25 to the reforming zone 30, it is first
31 passed to optional dehydrogenation unit 22. In dehydrogenation unit 22,

1 pentyltoluenes are contacted with a conventional dehydrogenation catalyst at
2 conventional dehydrogenation conditions. As a result, at least a portion of the
3 pentyltoluenes is dehydrogenated to form pentenyltoluenes.

4 Figure 2A is the same as Figure 2B, except that it does not show a
5 dehydrogenation unit 22 between the alkylation zone 20 and reforming
6 zone 30.

7 Figure 1 is the same as Figure 2B, except that it does not show TAME unit 5
8 and stream 10 is any C₅ olefin containing stream.

9 Figure 3 is the same as Figure 1, except that it shows a separation zone 40
10 following the reforming zone 30, shows a co-feed/diluent stream 17 to the
11 reforming zone 30, and shows a recycle stream 50 (e.g., for recycle of toluene
12 produced from reforming a C₇ naphtha co-feed) from the separation zone 40
13 to the alkylation zone 20. At least a portion of the DMN's is recovered as
14 stream 45.

15

16 Figure 4 is the same as Figure 1, except that it shows a co-feed/diluent
17 stream 17 to the reforming zone 30.

18

VII. ILLUSTRATIVE EMBODIMENTS

19

20

Example 1

21

Toluene Alkylation with TAME Raffinate and 2-Pentene over Zeolite Y

22 A catalyst was made by binding 80% Y zeolite and 20% alumina, extruding,
23 and calcining at 1100°F. This catalyst was crushed and sieved to give
24 particles in the 20/40 mesh size range. A 1.0 gram sample of the sized Y
25 zeolite catalyst was packing in a 1/2" OD tubular reactor such that the catalyst
26 was located in the isothermal region of a single zone electrically heated
27 furnace containing the reactor. Packing of inert alundum was placed above
28 and below the catalyst to hold it in place. A flow of dry nitrogen gas at

1 100 sccm was introduced and the catalyst heated to 392°F. The catalyst was
2 maintained at 392°F for 12 hours and then cooled to room temperature.
3 Toluene was then introduced into the reactor in the upflow mode at ca.
4 0.25 ml/minute. After about one hour, the pressure was increased to 175 psig
5 by means of a back pressure regulator. After the pressure stabilized, the
6 reactor was heated to 320°F. When the temperature stabilized, the toluene
7 flow was stopped and was replaced with a feed containing toluene and TAME
8 raffinate at a flow rate of 2.48 ml/hour. TAME raffinate is a stream consisting
9 mainly of C₅ species (containing about 35% pentenes) from the effluent of a
10 reactor making TAME (tertiary amyl methyl ether).

11 The feed composition was such that the toluene/pentenenes molar ratio was
12 equal to 10:1. Samples of the reactor effluent were periodically collected and
13 analyzed by gas chromatography. Results are shown in Table 1 below.
14 During much of the run, olefin conversion was essentially 100% (i.e.,
15 >99 mole %). At 287.5 hours into the run, the feed rate was increased to give
16 a WHSV of 3.2 h⁻¹. Olefin conversion decreased slightly. With a further
17 increase of WHSV to 4.2 h⁻¹ at 305 run hours, olefin conversion decreased
18 slightly again but still remained above 98 mole %. At 336 hours, the feed was
19 changed to a feed based on 2-pentene (i.e., a simulated feed containing
20 2-pentene, n-pentane, and toluene of the same approximate composition as
21 the TAME raffinate feed) and the WHSV increased to 6.0 h⁻¹, causing a
22 decrease in olefin conversion to 88.5 mole %. With a decrease in WHSV to
23 2.0 h⁻¹ at 359 hours, some of the conversion loss was restored and with a
24 further decrease in WHSV to 1.0 h⁻¹ at 380 hours, olefin conversion increased
25 to 98.5 mole %. The run was finally ended at ca. 480 hours. This example
26 shows the robustness and long catalyst life of a Y zeolite catalyst for the
27 alkylation of toluene with pentenes.

Table 1

Selected Yields and Selectivities of Toluene Alkylation with Pentenes at 320°F
(Selectivities Calculated on Mole % Olefin Consumed Basis)

Sample Number	Run Hours	WHSV, h ⁻¹	Pentene Source	Olefin Conv. Mole %	Pentyl-toluene Yield, Mole %	Dipentyl-toluene Yield, Mole %	Heavies ^a Yield, Mole %
13	160.5	2.1	TAME Raffinate	99.9	83.5	-	-
14	173	2.1	TAME Raffinate	99.9	75.1	6.7	4.1
18	280	2.1	TAME Raffinate	99.4	84.7	3.7	2.1
23	300	3.2	TAME Raffinate	98.7	85.9	3.0	2.7
24	324	4.2	TAME Raffinate	98.6	90.0	1.6	0.5
25	352	6.0	2-pentene	88.5	88.4	11.1	0.2
26	373	2.0	2-pentene	89.7	90.2	9.4	0.2
27	469	1.0	2-pentene	98.5	92.6	6.8	0.5

^a Calculated as pentene oligomer.

1

Example 2

2

Toluene Alkylation with TAME Raffinate over Various Zeolites

3

Other zeolitic catalysts were tested for the alkylation of toluene with pentenes.

4

The procedure for the alkylation runs was the same as described in

5

Example 1. Catalyst descriptions and experimental conditions for these runs

6

are listed in Table 2.

Table 2

Results of Alkylation Experiments with Pentenes over Zeolitic Catalysts

Run	Catalyst	Form	Catalyst Wt, g	Pentene source	WHSV h ⁻¹	Pressure, psig	Activation temp, °F	Alkylation temp, °F	Run length, hours	Olefin Conv, %
2A	Beta zeolite	Bound extrudate, crushed to 20/40 mesh	1.6	TAME Raffinate	2	175	392	320	160	~100
2B	SSZ-25	Pelletized powder, 20/40 mesh	1.7	TAME Raffinate	2	175	392	338	209	~100
2C	Al-SSZ- 33	Pelletized powder, 20/40 mesh	1.5	TAME Raffinate	2, 4 ^a	175	392	320	186	~100, ~75 ^b

^a WHSV increased to 4 at 40 run hours.^b Conversion at 4 h⁻¹ WHSV.

1 pentenes) were added dropwise over a six-hour period. The solution was
2 stirred magnetically at room temperature overnight. Subsequently,
3 0.66 grams of anhydrous AlCl_3 were added to the mixture. The temperature
4 was raised to 140°F for four hours. 100 ml of water were then added. The
5 aqueous layer was separated and discarded. The organic layer was washed
6 with additional water and dried with MgSO_4 . This reaction produced a
7 hydrocarbon mixture containing pentyltoluenes. The dried solution was
8 concentrated by removing most of the extra toluene by distillation. The
9 resulting distillate was analyzed by gas chromatography. About 48 grams of
10 pentyltoluenes were obtained.

11 Example 6

12 Toluene Alkylation with FCC C₅'s over Zeolite Y

13 An FCC C₅ sample was taken from the refinery FCC unit and had the
14 following approximate assay:

15	22.3%	isoamylene
16	21.3%	n-pentenes
17	0.03%	dienes
18	1.4%	butenes
19	1.5%	cyclopentene
20	53.5%	others (paraffins, naphthenes)

21 Toluene (2829 grams) and 463.3 grams of the above FCC C₅ sample were
22 blended. In a 1 liter autoclave, 750 ml of the above toluene/FCC C₅ blend
23 were combined with 13 grams of zeolite Y dehydrated in a N_2 flow at 595°F
24 for 3.5 hours. The resulting mixture was heated at 311°F under autogenous
25 pressure in a stirred autoclave for 1.75 hours. The mixture was then cooled to
26 ambient temperature and filtered. The pentyltoluenes were collected from the
27 reaction products by distillation. The resulting distillate was analyzed by gas
28 chromatography. About 96 grams of pentyltoluenes were obtained.

1 Example 7

2 Preparation of Reforming Catalysts

3 The representative non-zeolitic reforming catalyst tested for pentyltoluene
4 reforming to DMN's was a Pt-Re/Al₂O₃/Cl catalyst comprising approximately
5 0.3 wt.% Pt, 0.6 wt.% Re and 1.0 wt.% Cl. Preparation procedures of these
6 catalysts and their analogues with varying compositions are known to those
7 skilled in the art.

8 Example 8

9 Pretreatments of Reforming Catalysts

10 Depending on the properties of the catalysts used in the experiments of this
11 invention, a pretreatment step called sulfiding may be required to reduce the
12 hydrogenolysis activity. The sulfiding reaction of the Pt-Re/Al₂O₃/Cl catalyst
13 of Example 7 was conducted in down flow fixed bed reactor system. The
14 procedure is described as follows:

15 The catalyst was meshed to 24-42 chips and then loaded into stainless steel
16 tube reactors. The catalyst was first dried in a N₂ flow (300 ml/minute) from
17 room temperature to 400°F at a heating rate of 10°F/minute and kept at 400°F
18 for 30 minutes. The catalyst was then reduced as follows: the catalyst was
19 heated in a H₂ flow (300 ml/minute) from 400°F to 900°F at a heating rate of
20 5°F/minute and keeping at 900°F for 30 minutes. The catalyst was then
21 cooled to 800°F before starting the sulfiding reaction.

22 Sulfiding was accomplished by contacting a feed consisting of anhydrous n-
23 octane containing 200 ppm sulfur (as dimethyl disulfide) with the catalyst
24 using an H₂ carrier. The liquid feed flow rate was 0.43 ml/minute and the H₂
25 flow rate was 30 ml/minute. The sulfiding reaction was carried out at 800°F
26 and atmospheric pressure for 60 minutes.

1 After sulfiding, the catalyst was heated in a H₂ flow (300 ml/minute) from
2 800°F to 900°F within 10 minutes and then held at 900°F for an additional
3 30 minutes in order to remove the excess sulfur species occluded in the pores
4 and/or on the surface of the catalysts. Finally, the catalysts were cooled down
5 to room temperature within 5 hours in the same H₂ flow (300 ml/minute).

6 Example 9

7 Catalytic Testing Procedure for Reforming

8 Prior to the reforming testing, the catalysts (sulfided if required) were first
9 dried in a N₂ flow (100 ml/minute) from room temperature to 400°F at a
10 heating rate of 10°F/minute and kept at 400°F for 30 minutes. The catalysts
11 were subsequently heated in a H₂ flow (100 ml/minute) from 400°F to 900°F
12 at a heating rate of 5°F/minute and kept at 900°F for 30 minutes. Finally, the
13 catalysts were heated up or cooled down to the preset reforming temperature
14 (e.g., 870°F or 950°F). At the same time, the reactor system was pressurized
15 to the preset pressure (e.g., 50 or 130 psig) if pressures other than
16 atmospheric pressure were required. Meanwhile, the H₂ flow was adjusted to
17 the preset rate (e.g., 5 or 15 ml/minute).

18 The typical screening conditions for reforming were: 800-980°F, molar
19 H₂:pentyltoluenes ratio of 1:1 to 15:1 and pentyltoluenes WHSV of 0.1 to
20 10 h⁻¹. The reaction pressure was varied in the range of ~5-300 psig. The
21 feedstocks used were pentyltoluenes prepared over various catalysts such as
22 AlCl₃ or zeolite Y via the toluene alkylation with various C₅ olefins such as
23 1-pentene, TAME raffinate or FCC C₅'s.

24 The reforming products and unconverted pentyltoluenes were analyzed using
25 on-line GC (HP 5890 Series II equipped with a 50 meter long HP-1 or AT-35
26 capillary column), being capable of analyzing all resulting ethylnaphthalenes
27 (EN) and dimethylnaphthalenes (DMN) except for the separation of 2,6-DMN

1 and 2,7-DMN. The special design of the flow type reactor systems and the
2 use of the high temperature resistant valves and tubings guaranteed the
3 reliability of the on-line GC analysis. For the analysis of 2,6-DMN and
4 2,7-DMN, an off-line GC (HP 5880) which is coupled with a 120 meter long
5 capillary column (a 60 meter long AT-35 capillary column connected with a
6 60 meter long AT-50 capillary column) was used. In addition, GC/MS was
7 used also for product identification.

8 Example 10

9 Pentyltoluene Reforming on Amorphous Catalyst versus L Zeolite Catalyst

10 This example compares the catalytic performance of a representative
11 amorphous reforming catalyst to a zeolitic catalyst made from zeolite L
12 (Pt/Ba/K-L). The pentyltoluene feed prepared in Example 3 from 1-pentene
13 and toluene was reformed on the sulfided Pt-Re/Al₂O₃/Cl catalyst from
14 Example 7 and compared to an unsulfided Pt/Ba/K-L zeolite catalyst
15 containing ~0.7 wt.% Pt, ~5 wt.% Ba, and ~1.0 wt.% K. The reaction
16 conditions were as follows: 950°F, 50 psig and 200 psig, WHSV of 3 h⁻¹, and
17 a molar H₂-to-pentyltoluenes ratio of about 5:1. The on-line GC analysis
18 results collected at ~3 hours of reaction time are shown in Table 3. On the
19 amorphous catalyst, the resulting DMN's were essentially only those DMN
20 isomers which have the two methyl groups on different aromatic rings,
21 namely, 1,5-DMN, 1,6-DMN, 1,7-DMN, 2,6-DMN and 2,7-DMN. Only a very
22 small amount of ethylnaphthalenes (EN) was formed. The off-line GC
23 analysis showed that the ratio of 2,6/2,7-DMN was about 1:1. With Pt/Ba/K-L
24 zeolite catalyst, lower pentyltoluene conversion and lower DMN
25 yield/selectivity were observed. Because of such low DMN yields over
26 Pt/Ba/K-L zeolite catalyst, the selectivity of EN's and DMN's other than
27 1,5-DMN, 1,6-DMN, 1,7-DMN, 2,6-DMN and 2,7-DMN in the DMN products is
28 higher than with the Pt/Al₂O₃/Cl catalysts. The results show that amorphous
29 catalysts performed better for the formation of DMN's from pentyltoluenes.

Table 3

Reforming of Pentytoluenes on Amorphous Catalyst
versus Pt/Ba/K-L Zeolite Catalyst

Catalyst	Pt-Re/Al ₂ O ₃ /Cl		Pt/Ba/K-L	
Temperature, °F	950	950	950	950
Pressure, psig	50	200	50	200
WHSV, h ⁻¹	3	3	3	3
PT conversion, %	100	100	55	95
DMN yield, %	66	27	8	4
DMN selectivity, %	66	27	14.9	4.2

Example 11

Pentytoluene Reforming on Pt-Re/Al₂O₃/Cl Catalyst
at Various Temperatures and Pressures

The pentytoluene feed prepared in Example 3 from 1-pentene and toluene was reformed on the sulfided Pt-Re/Al₂O₃/Cl of Example 7 under various reaction conditions: 850-950°F, 50-130 psig, WHSV of 3 h⁻¹, and a molar H₂-to-pentytoluenes ratio of about 5:1. The on-line GC analysis results collected at ~3 hours of reaction time are shown in Table 4. The resulting DMN's were essentially only those DMN isomers which have the two methyl groups on different aromatic rings, namely, 1,5-DMN, 1,6-DMN, 1,7-DMN, 2,6-DMN and 2,7-DMN. Only a very small amount of ethylnaphthalenes (EN) was formed. The off-line GC analysis showed that the ratio of 2,6/2,7-DMN was about 1:1. The results show that higher temperature and lower pressure were favorable for the formation of DMN's.

Table 4

Reforming of Pentyltoluenes on Pt-Re/Al₂O₃/Cl
under Various Conditions (WHSV = 3 h⁻¹)

Condition		PT Conv., %	Yield, %				
T, °F	P, psi		1,5- DMN	1,6- DMN	1,7- DMN	2,6/2,7- DMN	Total DMN's
850	130	80	1.2	5.2	5.6	6.4	18.3
950	130	98	3.3	14.3	13.0	23.4	54.0
950	50	~100	6.1	19.3	18.5	22.1	66.0

Example 12

Pentytoluene Reforming on Pt-Re/Al₂O₃/Cl Catalyst
at Various Weight Hourly Space Velocities

The pentytoluene feed prepared in Example 3 from 1-pentene and toluene was reformed on the sulfided Pt-Re/Al₂O₃/Cl catalyst of Example 7 at 950°F, 50 psig, molar H₂-to-pentytoluenes ratio of about 6:1 and three different WHSV's: 1, 3 and 6 h⁻¹. The on-line GC analysis results collected at various reaction times are shown in Table 5. The resulting DMN's were essentially only those DMN isomers which have the two methyl groups on different aromatic rings, namely, 1,5-DMN, 1,6-DMN, 1,7-DMN, 2,6-DMN and 2,7-DMN. Only a very small amount of ethylnaphthalenes (EN) was formed. The off-line GC analysis showed that the ratio of 2,6/2,7-DMN was about 1:1. The results show that higher WHSV of the pentytoluene feed resulted in lower DMN yield and higher catalyst deactivation rate.

Table 5

Reforming of Pentyltoluenes on Pt-Re/Al₂O₃/Cl
under Various WHSV (950°F and 50 psig)

WHSV, h ⁻¹	1		3		6	
Reaction Time, h	3	63	3	64	3	19
PT Conversion, %	100	86	100	55	77	34
DMN Yield, %						
1,5-DMN	4.8	4.5	6.1	1.6	4.2	0.5
1,6-DMN	20.2	14.3	19.3	6.1	12.7	1.9
1,7-DMN	16.9	14.1	18.5	6.0	13.2	1.9
2,6/2,7-DMN	33.2	15.5	22.1	5.9	13.0	2.0
Total DMN's	75.1	48.4	66.0	19.6	43.1	6.3
DMN Selectivity, %	75.1	56.2	66.0	35.6	56	18.5

Example 13

Pentytoluene Reforming on Pt-Re/Al₂O₃/Cl Catalyst
at Various Weight Hourly Space Velocities

The pentytoluene feed prepared in Example 3 from 1-pentene and toluene was reformed on the sulfided Pt-Re/Al₂O₃/Cl catalyst of Example 7 at 950°F, ~5 psig, molar H₂-to-pentyltoluenes ratio of about 6:1, and three different WHSV's: 1, 0.5 and 0.25 h⁻¹. The results are shown in Table 6 in terms of pentytoluene conversion, DMN yield and DMN selectivity versus reaction time, respectively. The resulting DMN's were essentially only those DMN isomers which have the two methyl groups on different aromatic rings, namely, 1,5-DMN, 1,6-DMN, 1,7-DMN, 2,6-DMN and 2,7-DMN. Only a very small amount of ethylnaphthalenes (EN) was formed. The off-line GC analysis showed that the ratio of 2,6/2,7-DMN was about 1:1. The results show that lower WHSV of the pentytoluene feed improved the catalyst stability.

Table 6
Conversion of Pentyltoluenes on Pt-Re/Al₂O₃/Cl
under Various WHSV (950°F and ~5 psig)

WHSV, h ⁻¹	1			0.5			0.25		
Reaction Time, h	4	15	70	4	15	70	4	15	70
PT Conversion, %	100	72	-	100	95	76	100	99	82
DMN Yield, %									
1,5-DMN	6.9	2.5	-	4.9	5.2	2.7	4.3	4.5	3.4
1,6-DMN	19.8	9.5	-	18.5	16.9	10.7	17.0	16.9	13.6
1,7-DMN	23.8	9.9	-	20.3	20.3	11.1	19.6	19.0	13.7
2,6/2,7-DMN	32.2	13.2	-	35.8	29.6	14.9	35.2	33.2	22.0
Total DMN's	82.7	35.1	-	79.5	72.0	39.4	76.1	73.6	52.7
DMN Selectivity, %	82.7	48.8	-	79.5	75.8	40.4	76.1	74.3	64.3

Example 14
Pentyltoluene Reforming on Pt-Re/Al₂O₃/Cl Catalyst
at Various Pressures

The pentyltoluene feed prepared in Example 3 from 1-pentene and toluene was reformed on the sulfided Pt-Re/Al₂O₃/Cl catalyst of Example 7 at 950°F, 1 h⁻¹ WHSV, molar H₂-to-pentyltoluenes ratio of about 6:1, and two different pressures: ~5 and 50 psig. The results obtained under these two sets of conditions are shown in Table 5 (Example 12) and Table 6 (Example 13), respectively, in terms of pentyltoluene conversion, DMN yield and DMN selectivity versus reaction time, respectively. The results show that relatively higher pressure improved the catalyst stability.

Example 15
Pentyltoluene Reforming on Pt-Re/Al₂O₃/Cl Catalyst
under Various Conditions

The pentyltoluene feed prepared in Example 3 from 1-pentene and toluene was reformed on the sulfided Pt-Re/Al₂O₃/Cl catalyst of Example 7 at 870°F,

1 0.17 h⁻¹ WHSV, a molar H₂-to-pentyltoluenes ratio of about 6:1, and two
 2 different pressures: first, 100 psig (0–90 hours) and then 50 psig
 3 (90–240 hours). The experiment was conducted for about 240 hours without
 4 interruption. The results are shown Table 7 in terms of DMN yield versus
 5 reaction time. The pentyltoluene conversion was about 100% during the
 6 entire experiment. The resulting DMN's were essentially only those DMN
 7 isomers which have the two methyl groups on different aromatic rings,
 8 namely, 1,5-DMN, 1,6-DMN, 1,7-DMN, 2,6-DMN and 2,7-DMN. Only a very
 9 small amount of ethylnaphthalenes (EN) was formed. The off-line GC
 10 analysis showed that the ratio of 2,6/2,7-DMN was about 1:1. The results
 11 show that lower pressure improved the DMN yield. The experiment
 12 demonstrated also an unusually stable catalyst performance under these
 13 conditions.

14 Table 7

15 DMN Selectivity on Pt-Re/Al₂O₃/Cl under Various Conditions

Reaction Time, h	41	71	89	101	173	236
Pressure, psig	100			50		
DMN Yield, %						
1,5-DMN	0.9	1.0	1.0	1.9	2.0	2.1
1,6-DMN	5.2	5.4	5.4	9.9	10.5	10.6
1,7-DMN	4.5	4.6	4.8	8.4	8.6	8.5
2,6/2,7-DMN	9.7	10.2	10.5	18.4	19.2	18.9
Total DMN's	20.3	21.2	21.7	38.6	40.3	40.1

16
 17 Example 16

18 Reforming of Pentyltoluenes Prepared from Different C₅ Olefin Sources

19 This example compares the catalytic performance of the sulfided
 20 Pt-Re/Al₂O₃/Cl catalyst of Example 7 for reforming of pentyltoluene feeds
 21 prepared from toluene alkylation with C₅ olefins of various sources:

(1) 1-pentene (Example 3), (2) TAME Raffinate (Example 5) and (3) FCC C₅'s (Example 6).

The reaction conditions were as follows: 950°F, 50 psig, molar H₂:PT ratio of ~6:1, and WHSV of 1 h⁻¹. The on-line GC analysis results collected at ~3 hours of reaction time are shown in Table 8. The conversion of pentyltoluene feed was ~100%. The resulting DMN's were essentially only those DMN isomers which have the two methyl groups on different aromatic rings, namely, 1,5-DMN, 1,6-DMN, 1,7-DMN, 2,6-DMN and 2,7-DMN. Only a very small amount of ethylnaphthalenes (EN) was formed. The off-line GC analysis showed that the ratio of 2,6/2,7-DMN was about 1:1.

Table 8
Reforming of Pentyltoluenes Prepared from
Toluene Alkylation with C₅ Olefin(s) of Different Sources

C ₅ olefin source	1-pentene	TAME Raffinate	FCC C ₅ 's
DMN yield, %			
1,5-DMN	4.8	4.0	2.0
1,6-DMN	20.2	13.5	14.0
1,7-DMN	16.9	20.5	8.7
2,6/2,7-DMN	33.2	32.1	20.1
Total DMN's	75.1	70.1	44.8

Example 17

Pentyltoluene Reforming on Pt-Re/Al₂O₃/Cl Catalyst without Diluent/Co-feed

The pentyltoluene feed prepared in Example 6 from FCC C₅'s and toluene was reformed on the sulfided Pt-Re/Al₂O₃/Cl of Example 7 at 870°F, 50 psig, 0.17 h⁻¹ WHSV, and molar H₂-to-pentyltoluenes ratio of about 6:1. The results are shown in Table 9 in terms of DMN yield versus reaction time. The pentyltoluene conversion was ~100% during this experiment. The resulting

1 DMN's were essentially only those DMN isomers which have the two methyl
2 groups on different aromatic rings, namely, 1,5-DMN, 1,6-DMN, 1,7-DMN,
3 2,6-DMN and 2,7-DMN. Only a very small amount of ethylnaphthalenes (EN)
4 was formed. The off-line GC analysis showed that the ratio of 2,6/2,7-DMN
5 was about 1:1. The results when compared with the results of Example 15
6 (Table 7) show that DMN yield was lowered when the pentyltoluene feed
7 made from FCC C₅'s was used instead of the pentyltoluene feed made from
8 1-pentene (also see Example 16, Table 8).

Table 9

DMN Selectivity on Pt-Re/Al₂O₃/Cl with/without Diluent/Co-feed

Example	17			18			19			20		
	None			Benzene			Toluene			C ₇ naphtha		
Diluent/Co-feed	5	29	70	5	30	70	5	33	69	5	31	71
Reaction Time, h												
DMN Yield*, %												
1,5-DMN	1.2	1.3	1.1	1.8	2.1	2.0	1.8	2.3	2.3	2.0	2.3	2.4
1,6-DMN	6.0	6.7	5.7	9.0	10.4	9.7	9.0	10.9	10.5	9.6	10.6	10.4
1,7-DMN	5.4	5.9	5.0	7.8	8.7	8.1	7.6	9.2	8.9	8.3	9.1	9.1
2,6/2,7-DMN	14.1	14.7	12.6	16.9	19.0	17.5	16.7	19.5	18.5	18.3	19.4	18.4
Total DMN's	26.7	28.6	24.4	35.5	40.2	37.3	35.1	41.9	40.2	38.2	41.4	40.3

*DMN yield reported based on pentyltoluene feed, not total hydrocarbon feed.

Example 18

Pentyltoluene Reforming on Pt-Re/Al₂O₃/Cl Catalyst in the Presence of Benzene as Diluent

The pentytoluene feed prepared in Example 6 from FCC C₅'s and toluene was reformed on the sulfided Pt-Re/Al₂O₃/Cl catalyst of Example 7 at 870°F and 50 psig in the presence of benzene as diluent. In this case, the pentytoluene (PT) feed was blended with benzene at a weight ratio of PT to benzene of 1:2 and the molar H₂-to-pentytoluenes ratio was about 6:1. The WHSV of pentytoluenes was still kept to 0.17 h⁻¹. The reaction conditions were otherwise identical to those reported in Examples 17, 19 and 20. The results are shown in Table 9 in terms of DMN yield versus reaction time, together with the results obtained in Examples 17, 19 and 20. The pentytoluene conversion was ~100% during this experiment. The resulting DMN's were essentially only those DMN isomers which have the two methyl groups on different aromatic rings, namely, 1,5-DMN, 1,6-DMN, 1,7-DMN, 2,6-DMN and 2,7-DMN. Only a very small amount of ethylnaphthalenes (EN) was formed. The off-line GC analysis showed that the ratio of 2,6/2,7-DMN was about 1:1. Compared to the results from Example 17 (without diluent under otherwise identical conditions), the diluting of pentytoluenes with benzene significantly improved the DMN yield.

21 In addition, the results from a reference experiment using pure benzene as
22 feed under otherwise identical conditions indicated that benzene essentially
23 didn't undergo any chemical reactions (data not shown).

Example 19

Pentyltoluene Reforming on Pt-Re/Al₂O₃/Cl Catalyst in the Presence of Toluene as Diluent

28 The pentyltoluene feed prepared in Example 6 from FCC C₅'s and toluene
29 was reformed on the sulfided Pt-Re/Al₂O₃/Cl catalyst of Example 7 at 870°F

1 and 50 psig in the presence of toluene as diluent. In this case, the
2 pentytoluene (PT) feed was blended with toluene at a weight ratio of PT to
3 toluene of 1:2 and the molar H₂-to-pentytoluenes ratio was about 6:1. The
4 WHSV of pentytoluenes was still kept to 0.17 h⁻¹. The reaction conditions
5 were otherwise identical to those reported in Examples 17, 18 and 20. The
6 results are shown in Table 9 in terms of DMN yield versus reaction time,
7 together with the results obtained in Examples 17, 18 and 20. The
8 pentytoluene conversion was ~100% during this experiment. The resulting
9 DMN's were essentially only those DMN isomers which have the two methyl
10 groups on different aromatic rings, namely, 1,5-DMN, 1,6-DMN, 1,7-DMN,
11 2,6-DMN and 2,7-DMN. Only a very small amount of ethylnaphthalenes (EN)
12 was formed. The off-line GC analysis showed that the ratio of 2,6/2,7-DMN
13 was about 1:1. Compared to the results from Example 17 (without diluent
14 under otherwise identical conditions), the diluting of pentytoluenes with
15 toluene significantly improved the DMN yield, which was similar to the results
16 from Example 18 with benzene as diluent.

17 In addition, the results from a reference experiment using pure toluene as
18 feed under otherwise identical conditions indicated that toluene only slightly
19 underwent some chemical reactions (mainly <2% benzene detected) (data not
20 shown).

21 Example 20
22 Pentytoluene Reforming on Pt-Re/Al₂O₃/Cl Catalyst
23 in the Presence of a C₇ Naphtha as Co-Feed

24 The pentytoluene feed prepared in Example 6 from FCC C₅'s and toluene
25 was reformed on the sulfided Pt-Re/Al₂O₃/Cl catalyst of Example 7 at 870°F
26 and 50 psig in the presence of a C₇ naphtha as co-feed. The composition of
27 this C₇ naphtha co-feed is shown in Table 10. In this case, the pentytoluene
28 (PT) feed was blended with this C₇ naphtha at a weight ratio of PT to C₇'s of
29 1:2 and the molar H₂-to-pentytoluenes ratio was about 6:1. The WHSV of

1 pentyltoluenes was still kept to 0.17 h⁻¹. The reaction conditions were
 2 otherwise identical to those reported in Examples 17-19. The results are
 3 shown in Table 9 in terms of DMN yield versus reaction time, together with the
 4 results obtained in Examples 17-19. The pentyltoluene conversion was
 5 ~100% during this experiment. The resulting DMN's were essentially only
 6 those DMN isomers which have the two methyl groups on different aromatic
 7 rings, namely, 1,5-DMN, 1,6-DMN, 1,7-DMN, 2,6-DMN and 2,7-DMN. Only a
 8 very small amount of ethylnaphthalenes (EN) was formed. The off-line GC
 9 analysis showed that the ratio of 2,6/2,7-DMN was about 1:1. Compared to
 10 the results from Example 17 (without co-feed under otherwise identical
 11 conditions), the co-feeding of pentyltoluenes with C₇ naphtha significantly
 12 improved the DMN yield, which was similar to the results from Examples 18
 13 and 19 with benzene and toluene as diluents, respectively.

Table 10
Composition of the C₇ Naphtha

Composition:	wt. %
3,3,-dimethylpentane	0.72
Cyclohexane	0.64
2-methylhexane	20.63
2,3-dimethylpentane	8.76
1,1-dimethylcyclopentane	5.75
3-methylhexane	20.49
cis-1,3-dimethylcyclopentane	10.0
trans-1,2-dimethylcyclopentane	9.14
trans-1,3-dimethylcyclopentane	13.24
n-heptane	7.98
Methylcyclohexane	2.33
Ethylcyclopentane	0.05

1 The toluene yield obtained from the experimental run of this example was
2 about 32%. The resulting toluene consisted of the contributions of both C₇
3 reforming and pentyltoluene dealkylation. The toluene yield can be adjusted
4 by adjusting the PT-to-C₇ ratio in the reforming feed.

5 When the C₇ naphtha was co-fed, toluene was the major reforming product
6 from this co-feed. The advantage of using this kind of co-feed is that its
7 reforming product toluene can be used then within the integrated DMN
8 process for toluene alkylation with C₅ olefins in the alkylation step. It means
9 that it may only need a C₇ or C₆-C₁₂ naphtha stream for co-reforming to make
10 toluene and no extra toluene feed stream may be required. The integrated
11 process of this invention may require, therefore, only (1) a C₇ or C₆-C₁₂
12 naphtha stream (to make toluene) and (2) C₅ olefins (to alkylate the resulting
13 toluene for making pentyltoluenes which will be then reformed to DMN's with
14 toluene as major dealkylation product).

VIII. CLAIMS

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3 WHAT IS CLAIMED IS:

4 1. A method of making DMN, the method comprising:

5 a. contacting in an alkylation zone, at a temperature of from about
6 32°F to about 500°F and a pressure of from about ambient to about
7 500 psig, a toluene-containing stream with a TAME raffinate
8 stream, wherein the molar ratio of toluene in said toluene-
9 containing stream to pentenes in said TAME raffinate stream is
10 from about 4:1 to about 12:1; and the WHSV of said toluene-
11 containing stream and said TAME raffinate stream combined is
12 from about 1 h⁻¹ to about 8 h⁻¹, wherein said contacting is in the
13 presence of an acid alkylation catalyst selected from the group
14 consisting of aluminum chloride, acid clays, heteropolyacids, acidic
15 zeolites having a pore diameter of at least about 4.5 angstroms,
16 solid phosphoric acid catalysts, and mixtures thereof, wherein at
17 least a portion of said toluene and said TAME raffinate react to
18 form pentyltoluenes;

19 b. recovering from said alkylation zone at least a portion of said
20 pentyltoluenes;

21 c. passing a C₇ naphtha-containing stream and at least a portion of
22 said pentyltoluenes to a reforming zone containing an amorphous
23 platinum/alumina reforming catalyst comprising a metal selected
24 from the group consisting of a non-platinum Group VIII B metal,
25 rhenium, germanium, tin, lead, gallium, indium, and mixtures
26 thereof;



- 1 d. contacting in said reforming zone, said C₇ naphtha-containing
2 stream and said pentyltoluenes and said reforming catalyst, under
3 reforming conditions comprising a pressure from about ambient to
4 about 500 psig, a temperature from about 700°F to about 1000°F,
5 the molar ratio of hydrogen to C₇ naphtha-containing stream and
6 pentyltoluenes combined is from about 1:1 to about 15:1, the
7 pentyltoluenes WHSV is from about 0.1 h⁻¹ to about 10 h⁻¹, and the
8 C₇ naphtha to pentyltoluenes weight ratio is from about 0:1 to
9 about 1000:1, wherein:
- 10 (i) at least a portion of said pentyltoluenes is converted to
11 DMN's; and
- 12 (ii) at least a portion of said C₇ naphtha is converted to toluene;
- 13 e. recovering from said reforming zone at least a portion of said
14 DMN's; and
- 15 f. passing at least a portion of said toluene produced in step (d) to
16 said alkylation zone in step (a).
- 17 2. A method of making DMN's, comprising contacting in a reforming zone a
18 pentyltoluenes containing feed with an platinum-containing amorphous
19 reforming catalyst, comprising a metal selected from the group
20 consisting of a non-platinum Group VIIIB metal, rhenium, germanium,
21 tin, lead, gallium, indium, and mixtures thereof, at reforming conditions,
22 wherein at least a portion of said pentyltoluenes is converted to DMN's.
- 23 3. The method of claim 2 wherein said reforming catalyst further comprises
24 a support selected from the group consisting of alumina, silica, titania,
25 vanadia, chromia, zirconia, and mixtures thereof.



- 1 4. The method of claim 2 wherein said reforming catalyst further comprises
2 an alumina support.
- 3 5. The method of claim 2 wherein said reforming catalyst further comprises
4 a support selected from the group consisting of silica, titania, vanadia,
5 chromia, zirconia, and mixtures thereof.
- 6 6. The method of claim 2 wherein said reforming catalyst further comprises
7 rhenium.
- 8 7. The method of claim 2 wherein said reforming catalyst further comprises
9 germanium.
- 10 8. The method of claim 2 wherein said reforming catalyst further comprises
11 tin.
- 12 9. The method of claim 2 further comprising separating said DMN's from
13 any unreacted pentyltoluenes and recycling at least a portion of said
14 unreacted pentyltoluenes to said reforming zone.
- 15 10. The method of claim 2 wherein said reforming conditions comprise a
16 pressure from about ambient to about 500 psig.
- 17 11. The method of claim 2 wherein said reforming conditions comprise a
18 pressure from about ambient to about 300 psig.
- 19 12. The method of claim 2 wherein said reforming conditions comprise a
20 temperature from about 700°F to about 1000°F.
- 21 13. The method of claim 2 wherein said reforming conditions comprise a
22 pentyltoluenes WHSV of from about 0.01 h⁻¹ to about 100 h⁻¹.



- 1 14. The method of claim 2 wherein said reforming conditions comprise a
2 pentyltoluenes WHSV of from about 0.1 h^{-1} to about 10 h^{-1} and the molar
3 ratio of hydrogen to pentyltoluenes is from about 1:1 to about 15:1.
- 4 15. The method of claim 2, further comprising:
- 5 a. contacting, in an alkylation zone, at alkylation conditions, a toluene-
6 containing stream with a C_5 olefin containing stream in the
7 presence of an acid alkylation catalyst, wherein at least a portion of
8 said toluene and said C_5 olefins react to form pentyltoluenes; and
- 9 b. passing at least a portion of said pentyltoluenes to said reforming
10 zone.
- 11 16. The method of claim 15 wherein said C_5 olefin containing stream
12 comprises a TAME raffinate.
- 13 17. The method of claim 15 wherein said C_5 olefin containing stream
14 comprises an FCC C_5 stream.
- 15 18. The method of claim 15 wherein said alkylation conditions comprise a
16 pressure of from about ambient to about 500 psig, a temperature from
17 about 32°F to about 500°F , a toluene to C_5 olefin molar ratio of from
18 about 4:1 to about 12:1, and a WHSV of from about 1 h^{-1} to about 8 h^{-1} .
- 19 19. The method of claim 15 wherein said alkylation catalyst is a Y-zeolite
20 and said alkylation conditions comprise a temperature of from about
21 100°F to about 400°F , a pressure from about ambient to about 300 psig.
- 22 20. The method of claim 15 wherein said alkylation catalyst is AlCl_3 and said
23 alkylation conditions comprise a temperature of from about 32°F to
24 about 300°F , a pressure from about ambient to about 300 psig.



- 1 21. The method of claim 15 wherein said acid alkylation catalyst is selected
2 from the group consisting of aluminum chloride, acid clays, solid
3 phosphoric acid catalysts, heteropolyacids, acidic zeolites having a pore
4 diameter of at least about 4.5 angstroms, and mixtures thereof.
- 5 22. The method of claim 15 wherein said acid alkylation catalyst is selected
6 from the group consisting of Y zeolite, beta zeolite, mordenite, offretite,
7 omega, ferrierite, SSZ-20, SSZ-24, SSZ-25, SSZ-26, SSZ-31, SSZ-32,
8 SSZ-33, SSZ-35, SSZ-37, SSZ-42, SSZ-44, EU-1, NU-86, NU-87,
9 UTD-1, ZSM-5, ZSM-11, ZSM-12, ZSM-35, ZSM-48, MCM-22, MCM-36,
10 MCM-56, and mixtures thereof.
- 11 23. The method of claim 2 further comprising passing a diluent to said
12 reforming zone.
- 13 24. The method of claim 2 wherein said diluent is selected from the group
14 consisting of benzene, toluene, xylenes, C₅ naphtha, and mixtures
15 thereof.
- 16 25. The method of claim 2 wherein the weight ratio of said diluent to said
17 pentyltoluenes containing feed is from about 0:1 to about 1000:1.
- 18 26. The method of claim 2 further comprising co-feeding a C₆-C₁₂ naphtha-
19 containing stream to said reforming zone.
- 20 27. The method of claim 2 wherein the weight ratio of said co-feed to said
21 pentyltoluenes containing feed is from about 0:1 to about 1000:1.



- 1 28. A method of making DMN's, the method comprising:
- 2 a. passing a C₆–C₁₂ naphtha-containing stream and a pentyltoluenes-
- 3 containing stream to a reforming zone containing an amorphous
- 4 platinum/alumina reforming catalyst; and
- 5 b. contacting in said reforming zone, said C₆–C₁₂ naphtha-containing
- 6 stream and said pentyltoluenes and said reforming catalyst, under
- 7 reforming conditions, wherein:
- 8 (i) at least a portion of said pentyltoluenes is converted to
- 9 DMN's; and
- 10 (ii) at least a portion of said C₆–C₁₂ naphtha is converted to
- 11 aromatics.
- 12 29. The method of claim 28 wherein said C₆–C₁₂ naphtha consists
- 13 essentially of a C₇ naphtha and where at least a portion of said C₇
- 14 naphtha is converted to toluene, and further comprising passing at least
- 15 a portion of said toluene to an alkylation zone.
- 16 30. The method of claim 28 wherein said reforming catalyst further
- 17 comprises a metal selected from the group consisting of a non-platinum
- 18 Group VIII B metal, rhenium, germanium, tin, lead, gallium, indium, and
- 19 mixtures thereof.
- 20 31. The method of claim 28 wherein said reforming catalyst further
- 21 comprises rhenium.
- 22 32. The method of claim 28 wherein said reforming catalyst further
- 23 comprises germanium.



- 1 33. The method of claim 28 wherein said reforming catalyst further
2 comprises tin.
- 3 34. The method of claim 28 further comprising separating said DMN's from
4 any unreacted pentyltoluenes and recycling at least a portion of said
5 unreacted pentyltoluenes to said reforming zone.
- 6 35. The method of claim 28 wherein said reforming conditions comprise a
7 pressure from about ambient to about 500 psi.
- 8 36. The method of claim 28 wherein said reforming conditions comprise a
9 temperature from about 700°F to about 1000°F.
- 10 37. The method of claim 28 wherein said reforming conditions comprise a
11 pentyltoluenes WHSV of from about 0.01 h⁻¹ to about 100 h⁻¹.
- 12 38. The method of claim 28 wherein said reforming conditions comprise a
13 pentyltoluenes WHSV of from about 0.1 h⁻¹ to about 10 h⁻¹, the molar
14 ratio of hydrogen to C₆-C₁₂ naphtha-containing stream and
15 pentyltoluenes combined is from about 1:1 to about 15:1, and the weight
16 ratio of the C₆-C₁₂ naphtha-containing stream to pentyltoluenes is from
17 about 0:1 to about 1000:1.
- 18 39. The method of claim 29, further comprising:
- 19 a. contacting, in said alkylation zone, at alkylation conditions, a
20 toluene-containing stream with a C₅ olefin containing stream in the
21 presence of an acid alkylation catalyst, wherein at least a portion of
22 said toluene and said C₅ olefins react to form pentyltoluenes; and
- 23 b. passing at least a portion of said pentyltoluenes to said reforming
24 zone.



- 1 40. The method of claim 39 wherein said C₅ olefin containing stream
2 comprises a TAME raffinate.
- 3 41. The method of claim 39 wherein said C₅ olefin containing stream
4 comprises an FCC C₅ stream.
- 5 42. The method of claim 39 wherein said alkylation conditions comprise a
6 pressure of from about ambient to about 500 psig, a toluene to C₅ olefin
7 molar ratio of from about 4:1 to about 12:1, and a WHSV of from about
8 1 h⁻¹ to about 8 h⁻¹, and a temperature from about 32°F to about 500°F.
- 9 43. The method of claim 39 wherein said alkylation catalyst is a Y-zeolite
10 and said alkylation conditions comprise a temperature of from about
11 100°F to about 400°F, and a pressure from about ambient to about
12 300 psig.
- 13 44. The method of claim 39 wherein said alkylation catalyst is AlCl₃ and said
14 alkylation conditions comprise a temperature of from about 32°F to
15 about 300°F, and a pressure from about ambient to about 300 psig.
- 16 45. The method of claim 39 wherein said acid alkylation catalyst is selected
17 from the group consisting of aluminum chloride, acid clays, solid
18 phosphoric acid catalysts, heteropolyacids, acidic zeolites having a pore
19 diameter of at least about 4.5 angstroms, and mixtures thereof.
- 20 46. The method of claim 39 wherein said acid alkylation catalyst is selected
21 from the group consisting of Y zeolite, beta zeolite, mordenite, offretite,
22 omega, ferrierite, SSZ-20, SSZ-24, SSZ-25, SSZ-26, SSZ-31, SSZ-32,
23 SSZ-33, SSZ-35, SSZ-37, SSZ-42, SSZ-44, EU-1, NU-86, NU-87,
24 UTD-1, ZSM-5, ZSM-11, ZSM-12, ZSM-35, ZSM-48, MCM-22, MCM-36,
25 MCM-56, and mixtures thereof.



- 1 47. The method of claim 28 further comprising passing a diluent to said
2 reforming zone.
- 3 48. The method of claim 47 wherein said diluent is selected from the group
4 consisting of benzene, toluene, xylenes, C₅ naphtha, and mixtures
5 thereof.
- 6 49. The method of claim 47 wherein the weight ratio of said diluent to said
7 pentyltoluenes containing feed is from about 0:1 to about 1000:1.
- 8 50. The method of claim 28 wherein the weight ratio of said C₆–C₁₂ naphtha-
9 containing stream to said pentyltoluenes containing feed is from about
10 0:1 to about 1000:1.