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(54) Title: MANUFACTURE OF XYLENES FROM REFORMATE

(57) Abstract: A process is provided for the production of xylenes from reformat. The process is carried out by methylating the benzene, toluene, or both present in the reformat to produce a resulting product having a higher xylenes content than the reformat. Greater than equilibrium amounts of para-xylene can be produced by the process.

WO 2004/000767 A1

MANUFACTURE OF XYLENES FROM REFORMATE

BACKGROUND OF THE INVENTION

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Field of the Invention

This invention relates to a process for producing xylenes from reformat by methylating benzene and/or toluene present in the reformat to produce xylenes.

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Description of the Prior Art

Most aromatics production is based on the recovery of aromatics derived from catalytic reforming of naphtha. That process, using a feed containing a C₆+ hydrocarbons, typically produces a reformat comprised of C₆-C₈ aromatics along with paraffins and heavier aromatics.

15

Aromatics can also be produced by the dehydrocyclo-oligomerization of C₂-C₅ aliphatic hydrocarbons. That process typically produces a product comprised of benzene, toluene, xylenes, C₅+ paraffins, C₄ light paraffins, olefins, and unreacted C₂-C₅ aliphatic hydrocarbons.

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Another technique for producing aromatics involves the cracking of hydrocarbons such as by steam cracking or catalytic cracking. That process typically produces a product comprised of benzene, toluene, xylenes, C₆+ paraffins, and other hydrocarbons.

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The aromatics present in the reformat stream from a reformer or cracker will depend on the composition of the feedstock to the reformer or cracker, the type of reformer or cracker, and the operating conditions of the reformer or cracker. Normally, the aromatics present in the reformat stream will comprise benzene, toluene, a near equilibrium mixture of xylenes, ethylbenzene, and a mixture of nominally of C₉-C₁₀. Products of the reformat having the most value are benzene and xylenes. Of the xylene isomers, i.e., ortho-, meta- and para-xylene, the para-xylene is of particular value as a large volume chemical intermediate in a number of applications, such as the manufacture of terephthalic acid, which is an intermediate in the manufacturer of polyester.

The reformat is usually sent to an aromatics recovery complex where it undergoes several processing steps in order to recover high value products, e.g., xylenes and benzene, and to convert lower value products, e.g., toluene, into higher value products. For example, the aromatics present in the reformat are usually separated into different fractions by carbon number; e.g. benzene, toluene, xylenes, and ethylbenzene, etc. The C₈ fraction is then subjected to a processing scheme to make more high value para-xylene. Para-xylene is usually recovered in high purity from the C₈ fraction by separating the para-xylene from the ortho-xylene, meta-xylene, and ethylbenzene using selective adsorption or crystallization. The ortho-xylene and meta-xylene remaining from the para-xylene separation are isomerized to produce an equilibrium mixture of xylenes. The ethylbenzene is isomerized into xylenes or is dealkylated to benzene and ethane. The para-xylene is then separated from the ortho-xylene and the meta-xylene using adsorption or crystallization and the para-xylene-deleted-stream is recycled to extinction to the isomerization unit and then to

the para-xylene recovery unit until all of the ortho-xylene and meta-xylene are converted to para-xylene and recovered.

5 Toluene is typically recovered as a separate fraction and then may be converted into higher value products, e.g., benzene and/or xylenes. One toluene conversion process involves the disproportionation of toluene to make benzene and xylenes. Another process involves the hydrodealkylation of toluene to make benzene.

10 Both toluene disproportionation and toluene hydrodealkylation result in the formation of benzene. With the current and future anticipated environmental regulations involving benzene, it is desirable that the toluene conversion not result in the formation of significant quantities of benzene.

15 Xylenes can be produced by the methylation of toluene. Such a process is disclosed in U. S. Patent 3,965,207. One advantage of producing xylenes by this process is that the xylenes production does not result in the formation of benzene by-product.

20 In the past when it was desirable to methylate toluene, toluene present in the reformat has usually been first separated from the other hydrocarbons present in the reformat, such as by fractionation and extraction, before entering a methylation reactor. Such a separation requires substantial capital investment in
25 equipment, e.g., heat exchangers, high pressure separator, fractioners, etc. In addition, the reformat leaving the reformer is at elevated temperature and highly suitable for further conversion. With the separation of toluene from the reformat, the recovered toluene must
30 be heated again to conversion temperatures.

SUMMARY OF THE INVENTION

5 In accordance with the present invention, there is provided a process for producing xylenes from reformat, which process comprises:

(a) providing a reformat containing benzene, toluene or mixtures thereof in methylation reaction zone; and,

10 (b) methylating at least a portion of the benzene, toluene, or mixtures thereof present in said reformat in said methylation reaction zone with a methylating agent under conditions effective for the methylation and in the presence of a catalyst effective for the methylation to produce a resulting product having a higher xylenes content than said reformat.

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In another embodiment, the present invention provides a process for producing xylenes from reformat formed in an aromatization zone, which process comprises:

20 (a) forming reformat containing benzene, toluene or mixtures thereof in an aromatization zone;

(b) transferring at least a portion of the reformat from said aromatization zone to a methylation reaction zone; and,

25 (c) methylating at least a portion of the benzene, toluene, or mixtures thereof present in said reformat in said methylation reaction zone with a methylating agent under conditions effective for the methylation and in the presence of a catalyst effective for the methylation to produce a resulting product having a higher xylenes content than said reformat.

In a further embodiment, the present invention provides a multistage integrated process for upgrading a petroleum naphtha which comprises the steps of:

- (a) introducing the naphtha to an aromatization zone;
- 5 (b) reforming the naphtha under aromatization conditions and in the presence of a catalyst effective for the aromatization of the naphtha to produce a reformat containing benzene, toluene or mixtures thereof;
- (c) transferring at least a portion of said reformat from
10 said aromatization zone to a methylation reaction zone; and
- (d) methylating in said methylation reaction zone at least a portion of the benzene, toluene or mixtures thereof present in said reformat with a methylating agent under conditions effective for the methylation and in the presence of a catalyst effective for the
15 methylation to produce a resulting product having a higher xylenes content than said reformat.

An important feature of the present invention is that the aromatization zone and methylation zone can be in series flow
20 arrangement preferably without intermediate separation of the reformer effluent so that the two zones are operated under compatible conditions including hydrogen circulation rate and pressure.

The methylation reaction can occur in the liquid phase or
25 the vapor phase. Usually the reaction will occur in the vapor phase. The presence of the vapor phase in the reactor zone results in increased catalytic activity in the reactor zone and increased diffusion of molecules to the catalytic sites of the catalyst, e.g., pores of the molecular sieve. The expression "vapor phase", as used herein,
30 includes the presence of minor amounts of some liquid phase, e.g., less

than 10 percent by volume of liquid, as well as the substantial absence of liquid phase.

BRIEF DESCRIPTION OF THE DRAWING

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The Figure is a simplified process flow diagram, illustrating a preferred embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

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The term "aromatization", as used herein, shall mean the production of aromatics comprising benzene, toluene, or mixtures thereof by the conversion of non-aromatic hydrocarbons to aromatic hydrocarbons comprising benzene, toluene, or mixtures thereof. The term "aromatization", as used herein, shall also include the production of aromatics comprising benzene, toluene, or mixtures thereof by the cracking of heavy aromatic hydrocarbons to produce the aromatic hydrocarbons comprising benzene, toluene, or mixtures. Examples of aromatization processes include catalytic reforming of naphtha, dehydrocyclo-oligomerization of C₂-C₅ aliphatic hydrocarbons, steam cracking of hydrocarbons to produce aromatic hydrocarbons comprising benzene, toluene, or mixtures thereof, and the catalytic cracking of hydrocarbons to produce aromatic hydrocarbons comprising benzene, toluene, or mixtures thereof.

25

The term "reformate", as used herein, shall mean the product produced by "aromatization".

In a preferred embodiment of the invention as depicted in the Figure, a methylation unit is located inside the reforming loop with reformat methylation carried out without interstage separation.

5 Referring to the Figure, naphtha is directed via line 1 to heat exchanger 3 where the temperature of the naphtha is elevated. The naphtha feed can be either naphtha alone or the naphtha can be combined with toluene. Next, the heated naphtha is sent via line 5 to reformer heater 7 which elevates the temperature of the feed to a
10 temperature suitable for reforming. After heating, the naphtha is withdrawn via line 9 to aromatization reactor zone 11 where the naphtha is reformed into aromatic products. Although only one reactor zone is shown, there can be more than one reactor zone. The reformat is then withdrawn through line 13 to heat exchanger 15 where the
15 temperature of the reformat is adjusted for the methylation reaction. Next, the reformat is supplied via line 17 to methylation reaction zone 19. If desired, a stream of hydrocarbons comprised of benzene and/or toluene can be added to the reformat. The methylation reaction is usually carried out in the vapor phase. When carried out in the vapor
20 phase, if additional heat is necessary for the reformat to be in the vapor phase, the reformat can be heated to the vapor phase either before it enters the methylation reaction zone or after it has entered the methylation reaction zone. The methylating agent can be supplied to methylation reaction zone 19 via line 21. Usually the methylating
25 agent is supplied to the methylation reaction zone through more than one feed point. In methylation reaction zone 19, the toluene present in the reformat is methylated to form xylenes. Also, benzene present in the reformat can be methylated to form toluene which, in turn, can be methylated to form xylenes. Depending upon the composition of the
30 reformat, other reactions may also occur. For example, ethylbenzene

can be methylated to form para-ethyl-methylbenzene or dealkylated to form benzene, which in turn, can be methylated to form toluene which can be methylated to form xylenes. Also, any ethyl-methyl-benzene present in the reformat can be dealkylated to form toluene, which can be methylated to form xylenes. The catalyst used in the methylation reaction can be a catalyst that produces equilibrium amounts of xylene isomers or can be a catalyst that is selective to produce greater than equilibrium amounts of a desired xylene isomer, e.g., para-xylene. The methylated product is then sent via line 23 to heat exchanger 3. Heat exchanger 3 cools the methylated product and uses heat recovered from the methylated product to elevate the temperature of the naphtha supplied via line 1. Next, the methylated product is withdrawn through line 25 to heat exchanger 27 to further cool the methylated product for separation of hydrogen from the product. Next, the cooled methylated product is sent via line 29 to high pressure separator 31 where hydrogen is recovered. Hydrogen is removed via line 33 and sent to water dryer/oxygenate removal unit 35. It is important that the water and oxygenates not be recycled with the hydrogen into aromatization reaction zone 11. Hydrogen is removed from unit 35 via line 36 and either recycled back to the reforming unit or removed from the system via line 37. Water present in the methylated product can be removed from high pressure separator 31 via line 39. Next, the product is sent via line 41 to dryer 43 where remaining water and oxygenates are removed. The product is then sent via line 45 to separation block 47 where low pressure hydrogen, C₄ and C₅ are separated and removed via line 49. The resulting product, C₆+, is transferred via line 51 to distillation column 53 where C₆/C₇, including benzene and toluene, are removed overhead via line 55 for further processing. The C₈+ fraction is removed from the bottom of distillation column 53 via line 57 and further separated and converted in xylene

loop 59 to the desired molecules, e.g., para-xylene and other by-products. Practicing of the invention according to this embodiment allows sharing of the heat exchangers, furnace, compressor, phase separator, distillation, and the extraction hardware.

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Aromatization

Aromatization will usually be carried out by catalytic reforming of naphtha or the dehydrocyclo-oligomerization of C₂-C₅ aliphatics.

10

Dehydrocyclo-oligomerization involves converting C₂-C₅ aliphatic hydrocarbons to aromatic hydrocarbons. The process is carried out by contacting C₂-C₅ aliphatic hydrocarbons in an aromatization zone and in the presence of a catalyst suitable for dehydrocyclodimerization and under conditions effective to produce a aromatics product comprising benzene and/or toluene. The dehydrocyclodimerization process increases carbon chain length by oligomerization, promotes cyclization, and dehydrogenates cyclics to their respective aromatics.

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The feedstream used in the dehydrocyclo-oligomerization process will contain at least one aliphatic hydrocarbon containing 2 to about 5 carbon atoms. The aliphatic hydrocarbons may be open chain, straight chain, or cyclic. Examples such as hydrocarbons include ethane, ethylene, propane, propylene, n-butane, n-butenes, isobutane, isobutene, butadiene, straight and branch pentane, pentene, and pentyldiene. Dehydrocyclo-oligomerization conditions will vary depending on such factors as feedstock composition and desired conversion. A desired range of conditions for the dehydro-

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30

cyclodimerization of the aliphatic hydrocarbons to aromatics include a temperature from about 350° to about 650° C, a pressure from about 1 to about 100 atmospheres, and weight hour space velocity from about 0.2 to about 8. It is understood that, as the average carbon number of the feed increases, a temperature in the lower end of temperature range is required for optimum performance and conversely, as the average carbon number of the feed decreases, the higher the required reaction temperature.

The catalyst used in the dehydrocyclo-oligomerization reaction will preferably comprise an intermediate pore size molecular sieve. Intermediate pore size molecular sieves have a pore size from about 5 to about 7 Å and include, for example, AEL, AFI, MWW, MFI, MEL, MFS, MEI, MTW, EUO, MTT, HEU, FER, and TON structure type molecular sieves. These materials are described in "Atlas of Zeolite Structure Types", eds. W. H. Meier, D. H. Olson, and Ch. Baerlocher, Elsevier, Fourth Edition, 1996, which is hereby incorporated by reference. Examples of suitable intermediate pore size molecular sieves include ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-34, ZSM-35, ZSM-38, ZSM-48, ZSM-50, ZSM-57, MCM-22, MCM-49, MCM-56, and SAPO-5. Preferred molecular sieves are SAPO-11, as well as titanosilicate, gallosilicate, aluminosilicate, and gallium-containing aluminosilicate molecular sieves having a MFI structure.

Usually the molecular sieve will be combined with binder material resistant to the temperature and other conditions employed in the process. Examples of suitable binder material include clays, alumina, silica, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, and silica-titania, as well as ternary compositions, such as silica-alumina-thoria, silica-alumina-zirconia,

silica-alumina-magnesia and silica-magnesia-zirconia. The molecular sieve may also be composited with zeolitic material such as the zeolitic materials which are disclosed in U. S. Patent 5,993,642, which is hereby incorporated by reference.

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The relative proportions of molecular sieve and binder material will vary widely with the molecular sieve content ranging from between about 1 to about 99 percent by weight, more preferably in the range of about 10 to about 70 percent by weight of molecular sieve, and still more preferably from about 20 to about 50 percent.

10

To make enhanced amounts (greater than equilibrium amounts) of para-xylene (versus the other xylene isomers produced by the dehydrocyclo-oligomerization reaction), a molecular sieve catalyst, e.g., ZSM-5 catalyst, can be selectivated by the use of a selectivating agent.

15

Examples of compounds for selectivating the catalysts include treating the surface of the catalyst with compounds of phosphorus and/or various metal oxides such as alkaline earth metal oxides, e.g., calcium oxide, magnesium oxide, etc. rare earth metal oxides, lanthanum oxide, and other metal oxides such as boron oxide, titania, antimony oxide, and manganese oxide.

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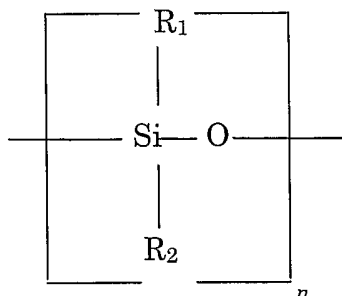
Selectivation may also be accomplished by depositing coke on the catalyst. The coke selectivation can be carried out during the methylation reaction such as by running the methylation reaction at conditions which allow the deposition of coke on the catalyst. Also, the catalyst can be preselectivated with coke such as by exposing the catalyst in the reactor to a thermally decomposable organic compound,

30

e.g., benzene, toluene, etc. at a temperature in excess of the decomposition temperature of said compound, e.g., from about 400°C to about 650°C, more preferably 425°C to about 550°C, at a WHSV in the range of from about 0.1 to about 20 lbs. of feed per pound of catalyst per hour, at a pressure in the range of from about 1 to about 100 atmospheres, and in the presence of 0 to about 2 moles of hydrogen, more preferably from about 0.1 to about 1 moles of hydrogen per mole of organic compound, and optionally in the presence of 0 to about 10 moles of nitrogen or another inert gas per mole of organic compound. This process is conducted for a period of time until a sufficient quantity of coke has deposited on the catalyst surface, generally at least about 2% by weight and more preferably from about 8 to about 40% by weight of coke.

15 Selectivation of the catalyst may also be accomplished using
organosilicon compounds. The silicon compounds may comprise a
polysiloxane include silicones, a siloxane, and a silane including
disilanes and alkoxysilanes.

20 Silicone compounds that can be used in the present
invention include the following:

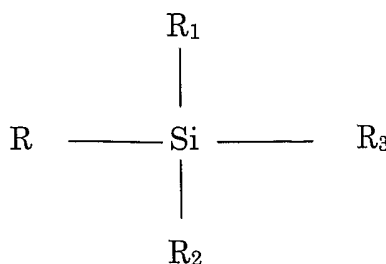


wherein R₁ is hydrogen, fluoride, hydroxy, alkyl, aralkyl, alkaryl or fluoro-alkyl. The hydrocarbon substituents generally contain from 1 to about 10 carbon atoms and preferably are methyl or ethyl groups. R₂ is

selected from the same group as R₁, and n is an integer of at least 2 and generally in the range of 2 to about 1000. The molecular weight of the silicone compound employed is generally between about 80 to about 20,000 and preferably about 150 to about 10,000. Representative
 5 silicone compounds include dimethylsilicone, diethylsilicone, phenylmethylsilicone, methyl hydrogensilicone, ethylhydrogensilicone, phenylhydrogensilicone, fluoropropylsilicone, ethyltrifluoropropylsilicone, tetrachlorophenyl methyl
 methylethylsilicone, phenylethylsilicone, diphenylsilicone,
 10 methyltrisilicone, tetrachlorophenylethyl silicone, methylvinylsilicone and ethylvinylsilicone. The silicone compound need not be linear but may be cyclic as for example hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, hexaphenyl cyclotrisiloxane and octaphenylcyclotetrasiloxane. Mixtures of these compounds may also
 15 be used as well as silicones with other functional groups.

Useful siloxanes and polysiloxanes include as non-limiting example hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethyl cyclopentasiloxane, hexamethyldisiloxane,
 20 octamethyltrisiloxane, decamethyltetrasiloxane, hexaethylcyclotrisiloxane, octaethylcyclo tetrasiloxane, hexaphenylcyclotrisiloxane and octaphenylcyclo-tetrasiloxane.

Useful silanes, disilanes, or alkoxysilanes include organic
 25 substituted silanes having the general formula:



wherein R is a reactive group such as hydrogen, alkoxy, halogen, carboxy, amino, acetamide, trialkylsilyoxy, R₁, R₂ and R₃ can be the same as R or can be an organic radical which may include alkyl of from 1 to about 40 carbon atoms, alkyl or aryl carboxylic acid wherein the organic portion of alkyl contains 1 to about 30 carbon atoms and the
5 aryl group contains about 6 to about 24 carbons which may be further substituted, alkylaryl and arylalkyl groups containing about 7 to about 30 carbon atoms. Preferably, the alkyl group for an alkyl silane is between about 1 and about 4 carbon atoms in chain length. Mixtures
10 may also be used.

The silanes or disilanes include, as non-limiting examples, dimethylphenylsilane, phenyltrimethylsilane, triethylsilane and hexamethyldisilane. Useful alkoxysilanes are those with at least one
15 silicon-hydrogen bond.

Selectivation of the catalyst can also be accomplished using a combination of coke and silicon applied by the procedures described above.

20 Catalytic reforming involves the production of aromatics from a C₆+ paraffinic feed, e.g., naphtha, by contacting the feed with a reforming catalyst under reforming conditions to produce a reaction product comprising aromatics and paraffins. The reformate is formed
25 under typical reforming conditions designed to promote dehydrogenation of naphthenes, isomerization of paraffinic hydrocarbons and dehydrocyclization of non-aromatic hydrocarbons.

Catalysts suitable for use in catalytic reforming include acidic reforming catalysts (bifunctional catalysts) and non-acidic reforming catalysts (monofunctional catalysts).

5 Acidic reforming catalysts usually comprise a metallic oxide support having disposed therein a Group VIII metal. Suitable metallic oxide supports include alumina and silica. Preferably, the acidic reforming catalyst comprises a metallic oxide support having disposed therein in intimate admixture a Group VIII metal (preferably
10 platinum) and a metal promoter, such as rhenium, tin, germanium, cobalt, nickel, iridium, rhodium, ruthenium and combinations thereof. More preferably, the acidic reforming catalyst comprises an alumina support, platinum, and rhenium or platinum and tin on an alumina support.

15 Non-acidic or monofunctional reforming catalysts will comprise a non-acidic molecular sieve, e.g., zeolite, and one or more hydrogenation/dehydrogenation components. Examples of suitable molecular sieves include MFI structure type, e.g., silicalite, and
20 molecular sieves having a large pore size, e.g., pore size from about 7 to 9 Angstroms. Examples of large pore molecular sieves include LTL, FAU, and *BEA structure types. Examples of specific molecular sieves include zeolite L, zeolite X, zeolite Beta, zeolite Y, and ETS-10.

25 The non-acidic catalysts will contain one or more hydrogenation/dehydrogenation metals, e.g., Group VII B metals, such as rhenium, and Group VIII metals, such as nickel, ruthenium, rhodium, palladium, iridium or platinum. The preferred Group VIII metal is platinum. Also, the nonacidic catalyst can contain a metal
30 promoter such as tin.

The amount of hydrogenation/dehydrogenation metal present on the non-acidic catalyst will usually be from about 0.1% to about 5% of hydrogenation/dehydrogenation metal based on the weight of the catalyst. The metal can be incorporated into the zeolite during synthesis of the zeolite, by impregnation, or by ion exchange of an aqueous solution containing the appropriate salt. By way of example, in an ion exchange process, platinum can be introduced by using cationic platinum complexes such as tetraammine-platinum (II) nitrate.

The non-acidic catalyst will usually include a binder. The binder can be a natural or a synthetically produced inorganic oxide or combination of inorganic oxides. Typical inorganic oxide supports which can be used include clays, alumina, and silica, in which acidic sites are preferably exchanged by cations that do not impart strong acidity.

The reforming process can be continuous, cyclic or semi-regenerative. The process can be in a fixed bed, moving bed, tubular, radial flow or fluid bed.

Conditions for reforming conditions include temperatures of at least about 400°C to about 600°C and pressures from about 50 psig (446 kPa) to about 500 psig (3,549 kPa), a mole ratio of hydrogen to hydrocarbons from 1:1 to 10:1 and a liquid hour space velocity of between 0.3 and 10.

Substantially any hydrocarbon feed containing C₆+ e.g., naphtha can be utilized. The naphtha will generally comprise C₆-C₉ aliphatic hydrocarbons. The aliphatic hydrocarbons may be straight or

branched chain acyclic hydrocarbons, and particularly paraffins such as heptane.

Toluene/Benzene Methylation

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The methylation reaction will usually occur in vapor phase. Reaction conditions for use in the present invention include temperatures from about 300° C to about 700° C and preferably about 400° C to about 700° C. The reaction is preferably carried out at a
10 pressure from about 1 to 1000 psig, and a weight hourly space velocity of between about 0.1 and about 200 and preferably between about 1 and about 100 weight of charge per weight of catalyst per hour. The molar ratio of toluene and benzene to methylating agent can vary and will usually be from about 0.1:1 to about 20:1. Preferred ratios for
15 operation are in the range of 2:1 to about 4:1. Hydrogen gas can be supplied to the reaction as an anticoking agent and diluent. The methylating agent is usually supplied to the methylation reaction zone through multiple feed points, e.g., 3-6 feed points.

20

Typical methylating agents include methanol, dimethylether, methylchloride, methylbromide, methylcarbonate, acetaldehyde, dimethoxyethane, acetone, and dimethylsulfide. The methylating agent can also be formed from synthesis gas, e.g., the agent can be formed from the H₂, CO, and/or CO₂ of synthesis gas. The
25 methylating agent can be formed from the synthesis gas within the methylation reaction zone. One skilled in the art will know that other methylating agents may be employed to methylate the benzene and/or toluene based on the description provided therein. Preferred methylating agents are methanol and dimethylether. Methanol is most
30 preferred.

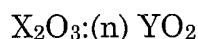
Catalysts suitable for use in the present invention include any catalyst that is effective for toluene or benzene methylation. The catalyst used in the process will usually comprise a crystalline molecular sieve.

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The catalyst used in the methylation reaction will preferably comprise an intermediate pore size molecular sieve. Intermediate pore size molecular sieves have a pore size from about 5 to about 7 Å and include, for example, AEL, AFI, MWW, MFI, MEL, MFS, MEI, MTW, EUO, MTT, HEU, FER, and TON structure type zeolites. These materials are described in "Atlas of Zeolite Structure Types", eds. W. H. Meier, D. H. Olson, and Ch. Baerlocher, Elsevier, Fourth Edition, 1996, which is hereby incorporated by reference. Examples of suitable intermediate pore size molecular sieves include ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-34, ZSM-35, ZSM-38, ZSM-48, ZSM-50, ZSM-57, MCM-22, MCM-49, MCM-56, and SAPO-5. Preferred molecular sieves are SAPO-11, as well as titanosilicate, gallosilicate, aluminosilicate, and gallium-containing aluminosilicate molecular sieves having a MFI structure.

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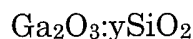
The intermediate pore size molecular sieve will generally be a composition having the following molar relationship:



wherein X is a trivalent element such as titanium, aluminum, iron, boron, and/or gallium and Y is a tetravalent element such as silicon, tin, and/or germanium; and n has a value greater than 12, said value being dependent upon the particular type of molecular sieve. When the intermediate pore size molecular sieve is a MFI structure type molecular sieve, n is preferably greater than 10 and preferably, from 20:1 to 200:1.

30

When the molecular sieve has a gallium silicate composition, the molecular sieve usually will be a composition having the following molar relationship:



5 wherein y is between about 20 and about 500. The molecular sieve framework may contain only gallium and silicon atoms or may also contain a combination of gallium, aluminum, and silicon.

Usually the molecular sieve will be incorporated with
10 binder material resistant to the temperature and other conditions employed in the process. Examples of suitable binder material include clays, alumina, silica, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, and silica-titania, as well as ternary compositions, such as silica-alumina-thoria, silica-alumina-zirconia,
15 silica-alumina-magnesia and silica-magnesia-zirconia. The molecular sieve may also be composited with zeolitic material such as the zeolitic materials which are disclosed in U.S. Patent 5,993,642.

The relative proportions of molecular sieve and binder
20 material will vary widely with the molecular sieve content ranging from between about 1 to about 99 percent by weight, more preferably in the range of about 10 to about 70 percent by weight of molecular sieve, and still more preferably from about 20 to about 50 percent.

25 The catalyst may also include at least one hydrogenation/dehydrogenation metal. Such metals can reduce the rate of deactivation of the catalyst. Reference to hydrogenation/dehydrogenation metal or metals is intended to encompass such metal or metals in the elemental state (i.e. zero valent) or in some other
30 catalytically active form such as an oxide, sulfide, halide, carboxylate

and the like. Such metals are known to persons skilled in the art and include, for example, one or more metals, and metals of Groups IIIA, IVA, VA, VIA, VIIA, VIII, IB, IIB, IIIB, IVB, VB, VIB, and VIIB of the Periodic Table of the Elements. Examples of suitable metals include
5 Group VIII metals (i.e., Pt, Pd, Ir, Rh, Os, Ru, Ni, Co and Fe), Group IVA metals (i.e., Sn and Pb), Group VA metals (i.e., Sb and Bi), and Group VIIB metals (i.e., Mn, Tc and Re). Noble metals (i.e., Pt, Pd, Ir, Rh, Os and Ru) are sometimes preferred.

10 When the catalyst used for the methylation reaction is a molecular sieve, the catalyst can be selectivated to enhance the amount of para-xylene produced by the methylation reaction by the use of a selectivating agent. Suitable selectivating agents include the selectivating agents disclosed earlier in this application for
15 selectivating dehydrocyclo-oligomerization molecular sieve catalysts.

Catalysts particularly suited for the methylation reaction are zeolite bound zeolite catalysts. These catalysts, as well as their method of preparation, are described in U. S. Patent 5,994,603, which
20 is hereby incorporated by reference. The zeolite bound zeolite catalysts will comprise first crystals of an acidic intermediate pore size first molecular sieve and a binder comprising second crystals of a second molecular sieve. Preferably, the zeolite bound zeolite catalyst contains less than 10 percent by weight based on the total weight of the first
25 and second zeolite of non-zeolitic binder, e.g., amorphous binder. An example of such a catalyst comprises first crystals of a MFI or MEL structure type, e.g., ZSM-5 or ZSM-11, and a binder comprising second crystals of MFI or MEL structure type, e.g., Silicalite 1 or Silicalite 2.

The amount of benzene/toluene converted to xylenes will depend on a number of factors including the make up of the reformat to be methylated, the methylation conditions, and the catalyst used. Usually, at least 5 weight percent of the benzene/toluene will be converted to xylenes. Preferably, at least 7 weight percent of the benzene/toluene will be converted to xylenes, and, more preferably, at least 30 weight percent of the benzene/toluene will be converted to xylenes.

The process of methylation of the benzene, toluene, or mixtures thereof present in the reformat can produce greater than equilibrium amounts of para-xylene. Preferably, the process will produce a xylene product containing greater than 30 weight percent para-xylene based on the total weight of xylenes produced by the process. More preferably, the process produces a xylene product containing greater than 60 weight percent para-xylene based on the total weight of the xylenes produced by the process. Most preferably, the process produces a xylene product containing greater than 80 weight percent para-xylene based on the total weight of the xylenes produced by the process.

The invention is further exemplified by the examples below, which are present to illustrate certain specific embodiments of the invention, but are not intended to be construed as to be restrictive of the spirit and scope thereof.

EXAMPLE 1

A simulated light naphtha reformat feed was subjected to toluene methylation. The catalyst used in the test comprised 1/16 inch

extrudates which contained 65 weight percent H-ZSM-5 and 35 weight percent silica binder. The catalyst had an alpha value of 330. The "alpha value" of a catalyst is an approximate indication of its catalytic cracking activity. The alpha test is described in U.S. Pat. No.

5 3,354,078 and in the *Journal of Catalysis*, Vol. 4, 522-529 (1965); Vol. 6, 278 (1966); and Vol. 61, 395 (1980), each incorporated herein by reference to that description.

10 The reformat feed used in the test had the composition given below:

TABLE 1

Component	Wt. %
C ₅ -	0.00
n-C ₆	18.58
i-C ₆	15.04
n-C ₇	4.30
i-C ₇	5.37
Benzene	15.32
Toluene	41.38
PX	0.00
MX	0.00
OX	0.00
EB	0.00
C ₉ +	0.00
Total	100

15

The test was carried out under the following conditions:

20

TABLE 2

Component	
WHSV (h^{-1})	1
MeOH/:Toluene [molar]	1
H ₂ :(MeOH+HCs) [molar]	1
Pressure (psig)	64
Temperature ($^{\circ}\text{F}$)	700

5 The test was carried out by loading the catalyst into a fixed
 bed reactor and heating the catalyst in flowing hydrogen at reactor
 temperature range from room temperature to 950° F for two hours.
 Next, the reformat was introduced into the reactor and the test was
 carried out under the conditions shown in Table 2. The results of the
 10 test are set forth below in Table 3.

TABLE 3

Component	Wt. %
C ₅ -	1.13
n-C ₆	16.58
i-C ₆	13.43
n- C ₇	3.87
i-C ₇	4.33
Benzene	11.06
Toluene	35.82
PX	2.59
MX	3.20
OX	3.76
EB	0.00
C ₉ +	4.23
Total	100

The results report in Table 3 shows that after toluene methylation, the content of the reformat increased from no xylenes being present to 9.49% xylenes. Also, the amount of para-xylene produced (27% para-xylene) was greater than an equilibrium amount (24% para-xylene).

EXAMPLE 2

A simulated light naphtha reformat feed was subjected to toluene methylation using a silicon-selectivated H-ZSM-5/silica bound catalyst.

The catalyst was selectivated by contacting H-ZSM-5/ silica bound (65 weight % H-ZSM-5 35 weight % silica) with dimethylphenylmethyl polysiloxane dissolved in decane and subsequently calcining the selectivated catalyst. The catalyst was treated with 3 additional silicon selectivation treatments using substantially the same procedure. The catalyst had an alpha value of approximately 300.

The reformat feed used in the test had the composition given below:

25

30

TABLE 4

Component	Wt. %
C ₅ -	0.00
n-C ₆	27.85
i-C ₆	3.64
n-C ₇	8.77
i-C ₇	0.05
Benzene	15.76
Toluene	43.93
PX	0.00
MX	0.00
OX	0.00
EB	0.00
C ₉ +	0.00
Total	100

The test was carried out under the following conditions:

TABLE 5

Component	
WHSV (h ⁻¹)	1
MeOH/:Toluene [molar]	1
H ₂ :(MeOH+HCs) [molar]	1
Pressure (psig)	200
Temperature (°F)	700

The test was carried out by loading the catalyst into a fixed bed reactor and heating the catalyst in flowing hydrogen at a reactor temperature range from room temperature to 950° F for two hours. Next, the reformat was introduced into the reactor and the test was

run at the conditions shown in Table 5. The results of the test are set forth below in Table 6.

TABLE 6

Component	Wt. %
C ₅ -	5.61
n-C ₆	21.32
i-C ₆	3.85
n- C ₇	5.44
i-C ₇	0.22
Benzene	11.39
Toluene	33.12
PX	2.66
MX	3.67
OX	2.36
EB	1.31
C ₉ +	9.05
Total	100

5

The results in Table 6 shows that after toluene methylation, the content of the reformat increased from no xylenes being present to 8.69 % xylenes. Also, the amount of para-xylene produced (31% para-xylene) was greater than an equilibrium amount (24% para-xylene).

10

EXAMPLE 3

A simulated light naphtha reformat feed was subjected to toluene methylation using a zeolite bound zeolite catalyst.

15

The catalyst comprised 70 wt.% H-ZSM-5 core crystals (average particle size of 3.5 microns) having a silica to alumina mole ratio of 75:1 and 30 wt.% ZSM-5 binder crystals having a silica to mole ratio of approximately 900:1. The catalyst was prepared by first

mixing the ZSM-5 core crystals with amorphous silica containing a trace amount of alumina and then extruding the mixture into a silica bound extrudate. Next, the silica binder of the extrudate was converted to the second zeolite by aging the aggregate at elevated temperatures in an aqueous solution containing a template and hydroxy ions sufficient to convert the silica to the binder crystals. The resulting zeolite bound zeolite was then washed, dried, calcined, and ion exchanged into the hydrogen form.

The reformat feed used in the test had the composition given below:

TABLE 7

Component	Wt. %
C ₅ -	0.00
n-C ₆	33.45
i-C ₆	3.88
n-C ₇	0.00
i-C ₇	0.00
Benzene	16.01
Toluene	46.66
PX	0.00
MX	0.00
OX	0.00
EB	0.00
C ₉ +	0.00
Total	100

The test was carried out under the following conditions:

TABLE 8

Component	
WHSV (h ⁻¹)	4
MeOH/:Toluene [molar]	1
H ₂ :(MeOH+HCs) [molar]	1
Pressure (psig)	200
Temperature (°F)	700

5 The test was carried out by loading the catalyst into a fixed
 bed reactor and heating the catalyst in flowing hydrogen at reactor
 temperature range from room temperature to 950° F for two hours.
 Next, the reformat was introduced into the reactor and the test was
 carried out at the conditions shown in Table 8. The results of the test
 10 are set forth below in Table 9.

TABLE 9

Component	Wt. %
C ₅ -	4.42
n-C ₆	26.69
i-C ₆	3.77
n- C ₇	0.00
i-C ₇	0.00
Benzene	13.21
Toluene	39.40
PX	2.18
MX	2.41
OX	1.79
EB	0.90
C ₉ +	5.24
Total	100

The results in Table 6 shows that after toluene methylation, the content of the reformat increased from no xylenes being present to 6.38 % xylenes. Also, the amount of para-xylene produced (34% para-xylene) was greater than an equilibrium amount (24% para-xylene).

5

EXAMPLE 4

A simulated light reformat, which would be formed by the dehydrocyclo-oligomerization of C₂-C₅ aliphatic hydrocarbons, was subjected to toluene methylation. The catalyst used in the test had an alpha value of approximately 22 and comprised 1/16 inch extrudates which contained 65 wt.% H-ZSM-23 having a silica to alumina mole ratio of 110:1 and 35 wt.% of alumina binder. The ZSM-23 was prepared according to U.S. Patent 4,076,842.

10
15

The reformat feed used in the test had the composition given below:

TABLE 10

Component	Wt. %
C ₅ -	0.00
n-C ₆	0.00
i-C ₆	0.00
n-C ₇	35.00
i-C ₇	5.00
Benzene	15.00
Toluene	45.00
PX	0.00
MX	0.00
OX	0.00
EB	0.00
C ₉ +	0.00
Total	100

The test was carried out under the following conditions:

TABLE 11

Component	
WHSV (h^{-1})	8
MeOH:Toluene [molar]	1/3
H ₂ :(MeOH+HCs) [molar]	2
Pressure (psig)	150
Temperature (°F)	932

5

The test was carried out by loading the catalyst into a fixed bed reactor and heating the catalyst in flowing hydrogen to the reaction temperature. Next, the reformat was introduced into the reactor and the test was run at the conditions shown in Table 11. The results of the test are set forth below in Table 12.

10

TABLE 12

Component	Wt. %
C ₅ -	19.25
n-C ₆	0.00
i-C ₆	0.00
n- C ₇	16.10
i-C ₇	4.65
Benzene	13.07
Toluene	41.45
PX	2.74
MX	1.83
OX	0.91
EB	0.00
C ₉ +	0.00
Total	100

The results in Table 12 show that after toluene methylation, the content of the reformat increased from no xylenes being present to 5.48 % xylenes. Also, the amount of para-xylene produced (50% para-xylene) was greater than an equilibrium amount (24% para-xylene).

EXAMPLE 5

A simulated full range naphtha reformat (without C₁-C₅ hydrocarbons) was subjected to toluene methylation using a silica selectivated ZSM-5 catalyst.

The ZSM-5 catalyst was selectivated using the procedure described above in Example 2. The catalyst had an alpha value of approximately 300.

The reformat feed used in the test had the composition given below:

TABLE 13

Component	Wt. %
C ₅ -	0.00
n-C ₆	33.12
i-C ₆	3.69
n-C ₇	0.00
i-C ₇	0.00
Benzene	15.85
Toluene	47.35
PX	0.00
MX	0.00
OX	0.00
EB	0.00
C ₉ +	0.00
Total	100

The test was carried out under the following conditions:

TABLE 14

Component	
WHSV (h^{-1})	9.2
MeOH/:Toluene [molar]	0.37
H ₂ :(MeOH+HCs) [molar]	2
Pressure (psig)	200
Temperature ($^{\circ}\text{F}$)	700

5

The test was carried out by loading the catalyst into a fixed bed reactor and heating the catalyst in flowing hydrogen at a reactor temperature range from room temperature to 950° F for two hours.

10 Next, the reformat was introduced into the reactor and the test was run at the conditions shown in Table 14. The product contained greater than 90% para-xylene based on the total amount of xylenes in the product.

EXAMPLE 6

15

A simulated light reformat, which would be formed by the dehydrocyclo-oligomerization of C₂-C₅ aliphatic hydrocarbons, was subjected to toluene methylation using a SAPO-11 catalyst. The catalyst had an alpha value of approximately 52 and its chemical analysis was Si_{1.1}Al₄₆P_{.44}. The SAPO-11 was prepared according to U.S. Patent 6,294,493.

20

The reformate feed used in the test had the composition given below:

TABLE 15

Component	Wt. %
C ₅ -	0.00
n-C ₆	0.00
i-C ₆	0.00
n-C ₇	35.00
i-C ₇	5.00
Benzene	15.00
Toluene	45.00
PX	0.00
MX	0.00
OX	0.00
EB	0.00
C ₉ +	0.00
Total	100

5

The test was carried out under the following conditions:

TABLE 16

Component	
WHSV (h ⁻¹)	8
MeOH:/Toluene [molar]	1/3
H ₂ :(MeOH+HCs) [molar]	2
Pressure (psig)	150
Temperature (°F)	932

10

The test was carried out by loading the catalyst into a fixed bed reactor and heating the catalyst in flowing hydrogen to the reaction temperature. Next, the reformat was introduced into the reactor and the test was run at the conditions shown in Table 16. The results of the test are set forth below in Table 17.

TABLE 17

Component	Wt. %
C ₅ -	19.25
n-C ₆	0.00
i-C ₆	0.00
n- C ₇	16.10
i-C ₇	4.65
Benzene	13.07
Toluene	41.45
PX	2.74
MX	1.83
OX	0.91
EB	0.00
C ₉ +	0.00
Total	100

The results in Table 17 shows that after toluene methylation, the content of the reformat increased from no xylenes being present to 5.8 % xylenes. Also, the amount of para-xylene produced was greater than 40% para-xylene.

What is claimed is:

1. A process for producing xylenes from reformate, which process comprises:

- 5 (a) providing a reformate containing benzene, toluene or mixtures thereof in methylation reaction zone; and,
- (b) methylating at least a portion of the benzene, toluene, or mixtures thereof present in said reformate in said methylation reaction zone with a methylating agent under vapor phase conditions effective
- 10 for the methylation and in the presence of a catalyst effective for the methylation to produce a resulting product having a higher xylenes content than said reformate.

2. A process recited in Claim 1, wherein said reformate is formed in

15 an aromatization zone and at least a portion of the reformate formed in said aromatization zone is transferred to said methylation reaction zone without interstage separation.

3. An integrated process for upgrading a petroleum naphtha which

20 comprises the steps of:

- (a) aromatizing naphtha in an aromatization zone under aromatization conditions and in the presence of a catalyst effective for the aromatization of the naphtha to produce a reformate containing benzene, toluene or mixtures thereof;
- 25 (b) transferring at least a portion of said reformate from said aromatization zone to a methylation reaction zone; and
- (c) methylating in said methylation reaction zone at least a portion of the benzene, toluene, or mixtures thereof present in said reformate with a methylating agent under conditions effective for the
- 30 methylation and in the presence of a catalyst effective for the

methylation to produce a resulting product having a higher xylenes content than said reformat;

5 wherein said reformat is transferred from said aromatization zone to said methylation reaction zone without interstage separation.

4. The process recited in Claim 3, wherein the methylation reaction is carried out in vapor phase.

10 5. The process recited in Claim 3 or 4, wherein said aromatization zone and methylation reaction zone are in series flow arrangement.

6. The process recited in any preceding claim, wherein said methylation conditions include a temperature from about 300° C to
15 about 700° C, a pressure from about 1 to 1000 psig, a weight hourly space velocity of between about 0.1 and about 200, a molar ratio of methylating agent to toluene between about 0.1:1 to about 20:1 and a weight hourly space velocity of between about 0.1 and about 200.

20 7. The process recited in any preceding claim, wherein said catalyst effective for methylation comprises an intermediate pore size molecular sieve.

8. The process recited in Claim 7, wherein said intermediate pore
25 size molecular sieve is selected from the group consisting of AEL, AFI, MWW, MFI, MEL, MFS, MEI, MTW, EUO, MTT, HEU, FER, and TON.

9. The process recited in Claim 7, wherein said intermediate pore
30 size molecular sieve is selected from the group consisting of ZSM-5,

ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-34, ZSM-35, ZSM-38, ZSM-48, ZSM-50, ZSM-57, MCM-22, MCM-49, MCM-56, and SAPO-11.

10. The process recited in Claims 7 to 9, wherein said catalyst
5 further comprises at least one hydrogenation/dehydrogenation metal.

11. The process recited in Claim 10, wherein said at least one
hydrogenation/dehydrogenation metal is a Group VIII metal.

10 12. The process recited in Claims 7 to 11, wherein said molecular
sieve is MFI or MEL.

13. The process recited in Claims 7 to 12, wherein said molecular
sieve further comprises a selectivating agent.

15 14. The process recited in Claim 13, wherein said selectivating agent
is selected from the group consisting of silica, coke, phosphorus,
alkaline earth metal oxide, rare earth metal oxides, lanthanum oxide,
boron oxide, titania, antimony oxide, manganese oxide, titania and
20 mixtures thereof.

15. The process recited in any preceding claim, wherein said
methyating agent is selected from the group consisting of methanol,
dimethylether, methylchloride, methylbromide, methylcarbonate,
25 acetaldehyde, dimethoxyethane, acetone, and dimethylsulfide.

16. The process recited in any preceding claim, wherein said
methyating agent is injected into said methylation reaction zone
through more than one feed point.

17. The process recited in any preceding claim, wherein said methylating agent is formed from synthesis gas.

5 18. The process recited in any preceding claim, wherein said reformat is formed by the catalytic reforming of naphtha.

10 19. The process recited in Claim 18, wherein said reforming is carried out a temperature in the range of from about 427°C to about 565°C, a pressure in the range of from about 50 psig (446 kPa) to about 500 psig (3,549 kPa), a mole ratio of hydrogen to hydrocarbons from 1:1 to 10:1 and a liquid hour space velocity of between 0.3 and 5 and in the presence of a catalyst suitable for the catalytic reforming of naphtha.

15 20. The process recited in Claim 18 or 19, wherein the catalyst suitable for catalysts reforming is a bifunctional catalyst.

20 21. The process recited in Claim 20, wherein said bifunctional catalyst is an acidic reforming catalyst comprising a metallic oxide support and a Group VIII metal.

22. The process recited in Claim 18 or 19, wherein the catalyst suitable for reforming is a monofunctional catalyst.

25 23. The process recited in Claim 22, wherein said monofunctional catalyst comprises a molecular sieve selected from the group consisting of zeolite L, zeolite X, zeolite Beta, zeolite Y, and ETS-10.

30 24. The process recited in Claim 22 or 23, wherein said monofunctional catalyst further comprises from about 0.1 to about 5% of at least one hydrogenation/dehydrogenation metal selected from the

group consisting of a Group VIII metal, Group VIIB metal, or mixtures thereof, based on the weight of the catalyst.

25. The process recited in Claims 1 to 17, wherein said reformat is
5 formed by the dehydrocyclo-oligomerization of C₂-C₅ aliphatics.

26. The process recited in Claim 25, wherein a catalyst comprising
an intermediate pore size molecular sieve is used in the dehydrocyclo-
oligomerization of C₂-C₅ aliphatics.

10

27. The process recited in Claim 26, wherein said molecular sieve
further comprises a selectivating agent.

28. The process recited in Claims 1 to 17, wherein said reformat is
15 formed by the cracking of hydrocarbons.

29. The process recited in Claim 28, wherein said cracking of
hydrocarbons is accomplished in a catalytic cracking process.

20 30. The process recited in Claim 28, wherein said cracking of
hydrocarbons is accomplished in a steam cracking process.

31. The process recited in any preceding claim, wherein at least 7
weight percent of the benzene and/or toluene present in said reformat
25 is converted to xylenes.

32. The process recited in any preceding claim, wherein the
resulting product contains greater than equilibrium amounts of para-
xylene.

30

33. The process recited in any preceding claim, wherein the resulting product contains more than 80 weight percent of para-xylene based on the total weight of the xylenes produced by said process.

5

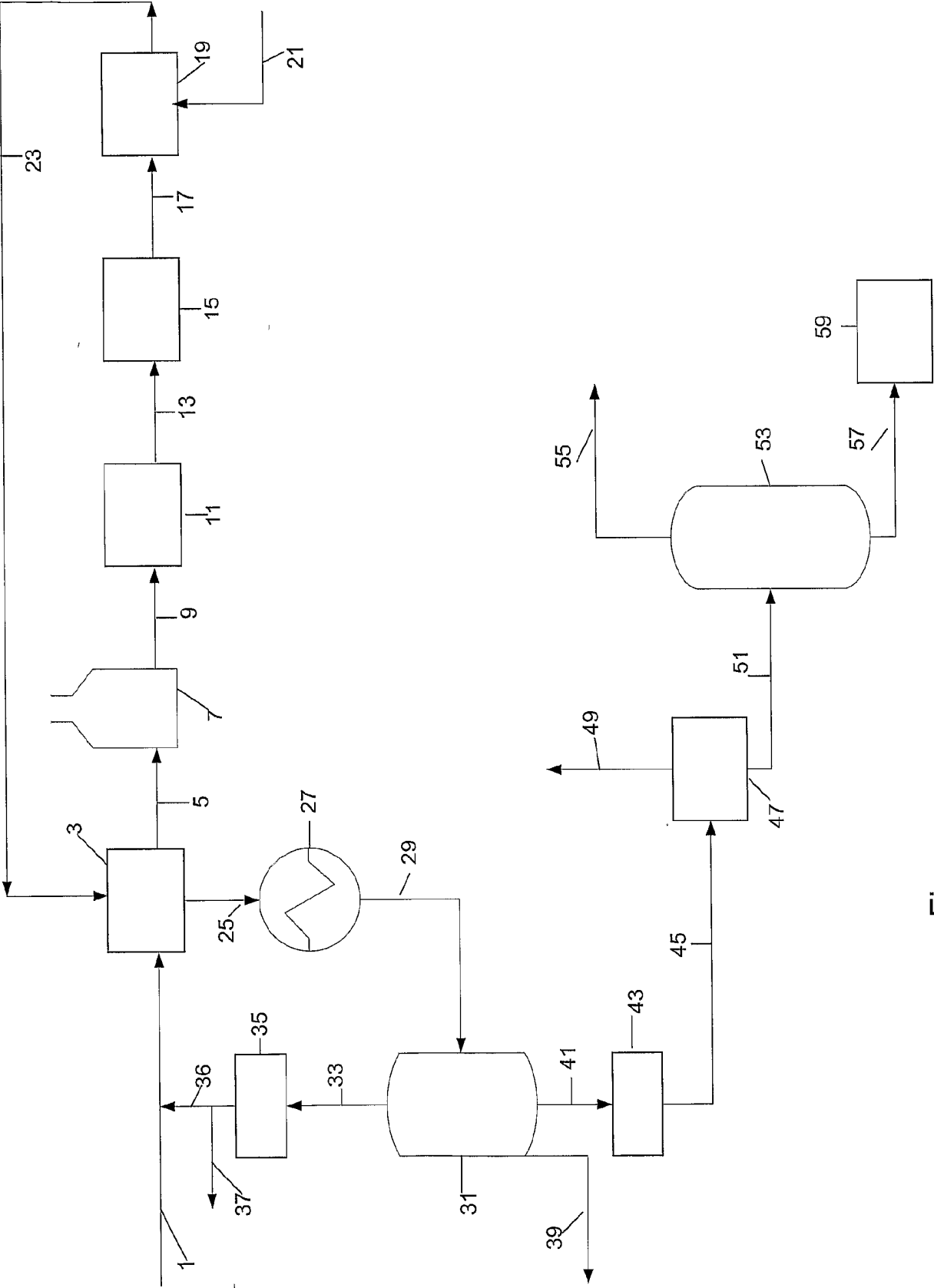
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Figure

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/19448

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C2/86 C07C15/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 388 156 B1 (HONG ZONGXUAN ET AL) 14 May 2002 (2002-05-14) the whole document ---	1-33
X	WO 96 16004 A (EXXON CHEMICAL PATENTS INC) 30 May 1996 (1996-05-30) the whole document ---	1-14, 18-30
X	US 3 965 209 A (BUTTER STEPHEN ALLAN ET AL) 22 June 1976 (1976-06-22) the whole document ---	1,4,6-15
Y		2,3,5, 16-33
X	US 3 965 210 A (CHU CHIN-CHIUN) 22 June 1976 (1976-06-22) *abstract; columns 2-5,8 and 11; the examples and te claims* ---	1,4,6-15
Y		2,3,5, 16-33
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

6 October 2003

Date of mailing of the international search report

13/11/2003

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/19448

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 994 603 A (MOHR GARY D ET AL) 30 November 1999 (1999-11-30)	1,4,6-15
Y	*abstract; column 2, paragraphs 3 and 4; column 3, last paragraph; columns 4-8; the examples and the claims*	2,3,5, 16-33
X	US 3 965 207 A (WEINSTEIN BENJAMIN) 22 June 1976 (1976-06-22)	1,4,6-15
Y	*abstract; column 1, last paragraph; column 2, lines 45-49; column 4, lines 57-70; column 5; column 8, lines 57-68; columns 9 and 11; the examples and the claims*	2,3,5, 16-33
X	WO 98 14415 A (WARE ROBERT ADAMS ;MOBIL OIL CORP (US); BROWN STEPHEN HAROLD (US);) 9 April 1998 (1998-04-09)	1,4,6-15
Y	the whole document	2,3,5, 16-33
X	US 4 670 616 A (DE SIMONE RICHARD E ET AL) 2 June 1987 (1987-06-02)	1,4, 6-15, 31-33
Y	*abstract; columns 2 and 4-7; the examples and the claims*	2,3,5, 16-30
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