

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
28 February 2002 (28.02.2002)

PCT

(10) International Publication Number
WO 02/16291 A1

- (51) International Patent Classification⁷: **C07C 2/66**, 15/073
- (74) Agents: **TYUS, Darryl, M.**; ExxonMobil Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 et al. (US).
- (21) International Application Number: PCT/US01/26201
- (81) Designated States (*national*): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (22) International Filing Date: 22 August 2001 (22.08.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
09/644,999 24 August 2000 (24.08.2000) US
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- (71) Applicant: **EXXONMOBIL CHEMICAL PATENTS, INC.** [US/US]; 5200 Bayway Drive, Baytown, TX 77520 (US).
- (72) Inventors: **ABICHANDANI, Jeevan, Sahib**; 3530 Emerald Falls Court, Houston, TX 77059 (US). **VENKAT, Chaya, R.**; 204 Bowstring Drive, Sedona, AZ 86336 (US). **MAZZONE, Dominick, N.**; 10 North Monroe Avenue, Wenonah, NJ 08090 (US).
- Published:**
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 02/16291 A1

(54) Title: PROCESS FOR ALKYLATING AROMATICS

(57) Abstract: A process for alkylating aromatics is provided which comprises contacting an aromatic-containing feed with alkylating agent in the presence of a silica-bound ZSM-5 zeolite catalyst, wherein the ZSM-5 has a crystal size no greater than 0.05 micron, said contacting being conducted under alkylating conditions to provide a product containing a monoalkylated aromatic fraction and a polyalkylated aromatic fraction, wherein the polyalkylated aromatic fraction contains at least 40 wt.% of the *para*-dialkylaromatic species. The polyalkylated aromatic fraction may be contacted with unsubstituted aromatic and a transalkylation catalyst under transalkylating conditions to provide a monoalkylated aromatic-rich stream, e.g., an ethylbenzene-rich stream.

PROCESS FOR ALKYLATING AROMATICS

Field of the Invention

The present invention relates to a process for alkylating aromatics.

5

Background of the Invention

The present invention is directed to a process for aromatics alkylation and in particular the alkylation of benzene with ethylene to provide ethylbenzene. Existing processes for producing ethylbenzene inherently produce polyalkylated species as well as the desired monoalkylated product. It is therefore normal to transalkylate the polyalkylated species with benzene to produce additional ethylbenzene either by recycling the polyalkylated species to the alkylation reactor or by feeding the polyalkylated species to a separate transalkylation reactor. It is, however, found that *para*-diethylbenzene (*p*-DEB) is easier to transalkylate than the *ortho* and *meta* isomers. There is therefore a continuing need for an aromatics alkylation process in which the polyalkylated by-products are rich in the *para* dialkyl component. Such a process would be particularly useful where it employs a catalyst which exhibits both alkylation and transalkylation activity under similar operating conditions inasmuch as the alkylation and transalkylation steps could be carried out in a single reactor with recycle of diethylbenzene.

10

15

20

U.S. Patent No. 3,751,504 to Keown et al. and U.S. Pat. No. 3,751,506 to Burress describe vapor phase alkylation of aromatic hydrocarbons with olefins, e.g., benzene with ethylene, in the presence of ZSM-5 zeolite.

U.S. Patent No. 4,086,287 to Kaeding et al. discloses a method for selectively ethylating monoalkyl benzenes to *para*-dialkyl substituted benzenes, such as *para*-diethylbenzene using ethylene as alkylating agent, over a zeolite-containing catalyst, e.g., ZSM-5, which may be incorporated in a matrix such as clay, silica, and/or metal oxides. The zeolite may be modified by incorporating a difficultly reducible oxide such as oxides of phosphorus, boron, and/or magnesium.

25

30

U.S. Patent No. 4,117,026 to Haag et al. discloses a method for selectively producing *para*-dialkyl substituted benzenes from monoalkyl substituted benzenes, e.g., toluene and C₂-C₁₅ olefin, over a zeolite-containing catalyst, e.g., ZSM-5, which may be incorporated in a matrix such as clay, silica, and/or metal
5 oxides. The reference further teaches enhanced *para*-xylene selectivity with large crystal ZSM-5 (1 micron) compared to small crystal ZSM-5 (0.03 micron).

U.S. Patent No. 4,169,111 to Wight teaches a method for producing ethylbenzene by alkylating benzene with ethylene in the presence of a catalyst, e.g., ZSM-5 which can be bound with mineral oxide binder, e.g., alumina gel or
10 silica gel. The process produces ethylbenzene and polyethylbenzenes. At least a portion of diethylbenzene fraction is recycled to the alkylation zone, while the remainder thereof plus the higher polyethylbenzenes are transalkylated with benzene to produce additional ethylbenzene.

U.S. Patent No. 5,243,117 to Chang et al. discloses a method for
15 selectively producing *para*-dialkyl substituted benzenes using a silica-modified non-organic ZSM-5 catalyst treated with an organosilicon compound, e.g., phenylmethylsilicone. The catalyst may be silica-bound.

U.S. Patent No. 5,530,170 to Beck et al. discloses a method for alkylating ethylbenzene with ethylene to selectively produce *para*-diethylbenzene using a
20 ZSM-5 zeolite catalyst which has been selectivated by multiple treatments with a siliceous material, e.g., dimethylsilicone. The catalyst may be silica-bound.

U.S. Patent No. 5,689,027 to Abichandani et al. discloses a method for converting ethylbenzene to compounds that may be removed from an aromatic hydrocarbon stream with minimal xylene loss using a silica bound intermediate
25 pore size zeolite that has been selectivated.

Summary of the Invention

According to the invention it has now been found that a silica bound, small crystal ZSM-5 zeolite catalyst provides a higher *p*-DEB content in total DEB
30 when used in the ethylation of benzene, thereby facilitating subsequent DEB conversion to ethylbenzene (EB). The novel catalyst also allows reduced

alkylation temperature and lower xylene make as compared to conventional catalysts.

In one aspect, the present invention relates to a process for alkylating aromatics which comprises contacting an aromatic-containing feed with alkylating agent in the presence of a silica-bound ZSM-5 zeolite catalyst, wherein the ZSM-5 has a crystal size no greater than 0.05 micron, e.g., 0.02 to 0.05 micron, said contacting being conducted under alkylating conditions to provide a product containing a monoalkylated aromatic fraction and a polyalkylated aromatic fraction, wherein the polyalkylated aromatic fraction contains at least 40 wt.% of the *para*-dialkylaromatic species.

In another aspect, the present invention relates to a process for preparing a monoalkylated aromatic compound which comprises:

- i) contacting an aromatic-containing feed in an alkylating reactor with alkylating agent in the presence of a silica-bound ZSM-5 zeolite alkylation catalyst, wherein the ZSM-5 has a crystal size of no greater than 0.05 micron, e.g., 0.02 to 0.05 micron, said contacting being conducted under alkylating conditions to provide a product containing a monoalkylated aromatic fraction and a polyalkylated aromatic fraction, wherein the polyalkylated aromatic fraction contains at least 40 wt% of the *para*-dialkylaromatic species;
- ii) separating the polyalkylated aromatic fraction from the product, and
- iii) contacting the polyalkylated aromatic fraction in the presence of unsubstituted aromatic and a transalkylation catalyst under transalkylating conditions to provide a monoalkylated aromatic-rich stream, e.g., an ethylbenzene-rich stream.

The reference in the present specification to the ZSM-5 having a "crystal size" of no greater than 0.05 micron is used to mean that the maximum dimension of the crystals in any direction is no greater than 0.05 micron.

The above and other objects, features and advantages of the present invention will be better understood from the following detailed descriptions, taken in conjunction with the accompanying drawings, all of which are given by illustration only, and are not limitative of the present invention.

Brief Description of the Drawings

Figure 1 compares catalyst aging during ethylbenzene production (% ethylene conversion over days on stream) for a silica-bound catalyst of the present invention and a conventional alumina-bound catalyst.

Figure 2 compares xylene make during ethylbenzene production (% ethylene conversion over days on stream) for a silica-bound catalyst of the present invention and a conventional alumina bound catalyst.

Figure 3 compares *para*-diethylbenzene/total diethylbenzene versus inlet temperature (°F) for a silica-bound catalyst of the present invention and a conventional alumina bound catalyst.

Figure 4 compares similar diethylbenzene conversions versus days on stream for a silica-bound catalyst of the present invention and a conventional alumina-bound catalyst.

Detailed Description of the Invention

The present invention is directed to a process for producing a monoalkylated aromatic compound, particularly ethylbenzene, by reacting an aromatic feedstock, particularly benzene, with alkylating agent, particularly ethylene, in the presence of a silica-bound ZSM-5 zeolite alkylation catalyst, wherein the ZSM-5 has a crystal size of no greater than, 0.05 micron, e.g., 0.02 to 0.05 micron. Preferably, the catalyst contains at least 70 wt.% zeolite. The resultant product contains both the desired monoalkylated aromatic compound and polyalkylated aromatic compounds rich in the *para*-dialkylaromatic species. The polyalkylated aromatic compounds are separated from the alkylation product and reacted with further aromatic feedstock in the presence of a transalkylation catalyst to produce additional monoalkylated product.

Alkylation and Transalkylation Catalysts

The alkylation catalyst used in the present invention comprises the zeolite ZSM-5 having a crystal size (maximum dimension in any direction) of no greater

than 0.05 micron, e.g., about 0.02 to about 0.05 micron. ZSM-5 is disclosed in U.S. Patent No. 3,702,886 and U.S. Patent Reissue No. 29,948 and a process for making small crystal ZSM-5 is disclosed in U.S. Patent No. 4,060,568, U.S. Patent No. 5,240,892 and U.S. Patent No. 5,369,071. The zeolite is composited
5 with a silica binder, preferably such that the alkylation catalyst contains at least 70 wt.% zeolite, more preferably 70-90 wt.%, and most preferably 75-85 wt.% zeolite, for example about 80 wt.% zeolite. The ZSM-5 employed preferably has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio greater than 40, more preferably from 60 to 80, and most preferably about 70.

10 Although it is known that zeolite catalysts can be selectivated by treatment with selectivating agents such as coke or organosilicon compounds, it is preferred that the alkylation catalysts employed in the present invention not be so treated. In particular, it is preferred that the ZSM-5 catalyst employed in the alkylation step of the invention has a Diffusion Parameter, $D/(r^2 \times 10^6)$, for 2,2-
15 dimethylbutane of at least 500, and more preferably from 700 to 2000, when measured at a temperature of 120°C and a 2,2-dimethylbutane pressure of 60 torr (8 kPa), wherein D is the diffusion coefficient (cm^2/sec) and r is the crystal radius (cm). The required Diffusion Parameters can be derived from sorption measurements provided the assumption is made that the plane sheet model
20 describes the diffusion process. Thus for a given sorbate loading Q, the value Q/Q_∞ , where Q_∞ is the equilibrium sorbate loading, is mathematically related to $(Dt/r^2)^{1/2}$ where t is the time (sec) required to reach the sorbate loading Q. Graphical solutions for the plane sheet model are given by J. Crank in "The Mathematics of Diffusion", Oxford University Press, Ely House, London, 1957.

25 The transalkylation catalyst used in the process of the invention is preferably ZSM-5 and most preferably the same silica-bound, small crystal ZSM-5 used as the alkylation catalyst. Alternative transalkylation catalysts include other medium pore zeolites having a Constraint Index of 2-12 (as defined in U.S. Patent No. 4,016,218), such as ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, and
30 ZSM-48. ZSM-11 is described in detail in U.S. Patent No. 3,709,979. ZSM-12 is described in U.S. Patent No. 3,832,449. ZSM-22 is described in U.S. Patent No.

4,556,477. ZSM-23 is described in U.S. Patent No. 4,076,842. ZSM-35 is described in U.S. Patent No. 4,016,245. ZSM-48 is more particularly described in U.S. Patent No. 4,234,231.

In addition, large-pore zeolites, including those zeolites having a Constraint Index less than 2, are suitable for use as the transalkylation catalyst in the process of the invention. Suitable large pore zeolites include zeolite Beta, zeolite Y, Ultrastable Y (USY), Dealuminized Y (Deal Y), mordenite, ZSM-3, ZSM-4, ZSM-18, and ZSM-20. Zeolite ZSM-14 is described in U.S. Patent No. 3,923,636. Zeolite ZSM-20 is described in U.S. Patent No. 3,972,983. Zeolite Beta is described in U.S. Patent Nos. 3,308,069, and Re. No. 28,341. Low sodium Ultrastable Y molecular sieve (USY) is described in U.S. Patent Nos. 3,293,192 and 3,449,070. Dealuminized Y zeolite (Deal Y) may be prepared by the method found in U.S. Patent No. 3,442,795. Zeolite UHP-Y is described in U.S. Patent No. 4,401,556.

Other acidic solid oxides, which may be used to catalyze the present transalkylation reaction, include MCM-22, PSH-3, SSZ-25, MCM-36, MCM-49 and MCM-56. MCM-22 and its use to catalyze the synthesis of alkylaromatics, including ethylbenzene, is described in U.S. Patent Nos. 4,992,606; 5,077,445; and 5,334,795. PSH-3 is described in U.S. Patent No. 4,439,409. SSZ-25 and its use in aromatics alkylation are described in U.S. Patent No. 5,149,894. MCM-36 is described in U.S. Patent Nos. 5,250,277 and 5,292,698. U.S. Patent No. 5,258,565 describes the synthesis of alkylaromatics, including ethylbenzene, using a catalyst comprising MCM-36. MCM-49 is described in U.S. Patent No. 5,236,575. The use of MCM-49 to catalyze the synthesis of alkylaromatics, including ethylbenzene, is described in U.S. Patent Nos. 5,493,065 and 5,371,310. MCM-56 is described in U.S. Patent No. 5,362,697. The use of MCM-56 to catalyze the synthesis of alkylaromatics including ethylbenzene is described in U.S. Patent Nos. 5,557,024 and 5,453,554.

Reactants

The reactants used in the process of the invention include an alkylatable aromatic compound and an alkylating agent.

The term "aromatic" in reference to the alkylatable compounds which are useful herein is to be understood in accordance with its art-recognized scope which includes alkyl substituted and unsubstituted mono- and polynuclear compounds. Compounds of an aromatic character which possess a heteroatom are also useful provided they do not act as catalyst poisons under the reaction conditions selected.

Substituted aromatic compounds which can be alkylated herein must possess at least one hydrogen atom directly bonded to the aromatic nucleus. The aromatic rings can be substituted with one or more alkyl, aryl, alkaryl, alkoxy, aryloxy, cycloalkyl, halide, and/or other groups which do not interfere with the alkylation reaction.

Suitable aromatic hydrocarbons include benzene, naphthalene, anthracene, naphthacene, perylene, coronene, and phenanthrene, with benzene being preferred.

Generally the alkyl groups which can be present as substituents on the aromatic compound contain from about 1 to 22 carbon atoms and usually from about 1 to 8 carbon atoms, and most usually from about 1 to 4 carbon atoms.

Suitable alkyl substituted aromatic compounds include toluene, xylene, isopropylbenzene, normal propylbenzene, alpha-methylnaphthalene, ethylbenzene, mesitylene, durene, cymenes, butylbenzene, pseudocumene, *o*-diethylbenzene, *m*-diethylbenzene, *p*-diethylbenzene, isoamylbenzene, isohexylbenzene, pentaethylbenzene, pentamethylbenzene; 1,2,3,4-tetraethylbenzene; 1,2,3,5-tetramethylbenzene; 1,2,4-triethylbenzene; 1,2,3-trimethylbenzene, *m*-butyltoluene; *p*-butyltoluene; 3,5-diethyltoluene; *o*-ethyltoluene; *p*-ethyltoluene; *m*-propyltoluene; 4-ethyl-*m*-xylene; dimethylnaphthalenes; ethylnaphthalene; 2,3-dimethylantracene; 9-ethylantracene; 2-methylantracene; *o*-methylantracene; 9,10-dimethylphenanthrene; and 3-methyl-phenanthrene. Higher molecular weight alkylaromatic hydrocarbons can also be used as starting materials and include aromatic hydrocarbons such as are produced by the alkylation of aromatic hydrocarbons with olefin oligomers. Such products are frequently referred to in

the art as alkylate and include hexylbenzene, nonylbenzene, dodecylbenzene, pentadecylbenzene, hexyltoluene, nonyltoluene, dodecyltoluene, pentadecyltoluene, etc. Very often alkylate is obtained as a high boiling fraction in which the alkyl group attached to the aromatic nucleus varies in size from about
5 C₆ to about C₁₂. When cumene or ethylbenzene is the desired product, the present process produces acceptably little by-products such as xylenes. The xylenes make in such instances may be less than about 500 ppm.

Reformat containing substantial quantities of benzene, toluene and/or xylene constitutes a particularly useful feed for the alkylation process of this
10 invention.

The alkylating agents useful in the process of this invention generally include any aliphatic or aromatic organic compound having one or more available alkylating aliphatic groups capable of reaction with the alkylatable aromatic compound, preferably with the alkylating group possessing from 1 to 5 carbon
15 atoms. Examples of suitable alkylating agents are olefins such as ethylene, propylene, the butenes, and the pentenes; alcohols (inclusive of monoalcohols, dialcohols, trialcohols, etc.) such as methanol, ethanol, the propanols, the butanols, and the pentanols; aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, and n-valeraldehyde; and alkyl halides such as
20 methyl chloride, ethyl chloride, the propyl chlorides, the butyl chlorides, and the pentyl chlorides, and so forth.

Mixtures of light olefins are especially useful as alkylating agents in the alkylation process of this invention. Accordingly, mixtures of ethylene, propylene, butenes, and/or pentenes which are major constituents of a variety of
25 refinery streams, e.g., fuel gas, gas plant off-gas containing ethylene, propylene, etc., naphtha cracker off-gas containing light olefins, refinery FCC propane/propylene streams, etc., are useful alkylating agents herein. For example, a typical FCC light olefin stream possesses the following composition:

	<u>Wt. %</u>	<u>Mole %</u>
Ethane	3.3	5.1
Ethylene	0.7	1.2
Propane	4.5	15.3
5 Propylene	42.5	46.8
Isobutane	12.9	10.3
n-Butane	3.3	2.6
Butenes	22.1	18.32
10 Pentanes	0.7	0.4

Preferably, the reactants in the process of the invention are benzene and ethylene and the desired reaction product is ethylbenzene.

Reaction Conditions

15 The alkylation and transalkylation reactions may take place under liquid phase conditions or vapor phase conditions or mixed liquid/vapor phase conditions. For example, one of these reactions may take place under liquid phase or mixed liquid/vapor phase conditions, while the other reaction takes place under vapor phase conditions. However, both reactions preferably take place under vapor phase
20 conditions.

Particular conditions for carrying out the vapor phase alkylation of benzene with ethylene may include a temperature of from about 650 to 900°F (343 to 482°C), e.g., from about 700 to 850°F (371 to 454°C), a pressure of about atmospheric to about 3000 psig, e.g., from about 25 psig to about 450 psig, a WHSV
25 based on ethylene of from about 0.5 to about 10.0 hr⁻¹, e.g., about 0.5 to about 2.0 hr⁻¹ and a mole ratio of benzene to ethylene of from 1:1 to 30:1.

Liquid phase alkylation of benzene with ethylene may be carried out at temperatures between 300 and 650°F (150 to 340°C.) usually in the range of 400 to 520°F (205 to 270°C). Pressures during the liquid phase alkylation of benzene with
30 ethylene may be as high as about 3000 psig (20875 kPa) although generally will not exceed 1000 psig (7000 kPa). The reaction may be carried out in the absence of hydrogen and accordingly the prevailing pressures are those of the reactant species. The space velocity may be from about 0.1 to 20 WHSV, based on the ethylene feed. Preferred space velocities for the liquid phase alkylation of benzene with ethylene

include ranges, for example, from about 0.5 to about 3 WHSV, e.g., from about 0.75 to 2.0 WHSV, (ethylene). The ratio of the benzene to the ethylene in the alkylation reactor may be from 1:1 to 30:1 molar, normally about 5:1 to 20:1 molar, and in most cases from about 5:1 to 10:1 molar.

- 5 Particular conditions for carrying out the vapor phase transalkylation of benzene with polyethylbenzenes may include a temperature of from about 260°C to about 482°C, e.g., from about 370 to 450°C, a pressure of from about atmospheric to about 3000 psig, e.g., from about 50 to about 500 psig, a WHSV based on the weight of the total vapor feed to the reaction zone of from about 1 to about 50 hr⁻¹
10 and a mole ratio of benzene to polyethylbenzene of from about 1 to about 50.

- Particular conditions for carrying out the liquid phase transalkylation of benzene with polyethylbenzenes may include a temperature of from about 150°C to about 260°C, a pressure of 7000 kPa or less, a WHSV based on the weight of the total liquid feed to the reaction zone of from about 0.5 to about 2.0 hr⁻¹ and a mole
15 ratio of benzene to polyethylbenzene of from 1:1 to 30:1.

- The process of the present invention, which employs silica-bound ZSM-5 zeolite catalyst composite of no greater than 0.05 micron, e.g., 0.02-0.05 micron, zeolite crystal size, as the alkylation catalyst, provides certain advantages over prior art processes. In particular, the polyalkylated fraction of the alkylation
20 product contains at least 40 wt.% of the *para*-dialkylaromatic species. Moreover, the *para*-diethylbenzene content of the alkylation product is greater than 45 wt.%, preferably greater than 50 wt.% of the total diethylbenzene in the product. The high *para*-diethylbenzene content facilitates subsequent transalkylation.

- The alkylation step of the process of the invention may be effected at a
25 start of cycle temperature 20-30°F lower, e.g., well below 750°F, than conventional vapor phase EB processes possibly owing to enhanced coke resistance of the silica-bound catalyst as compared to comparable alumina-bound catalyst composite. The lower start of cycle temperature provides longer cycle lengths.

- 30 Moreover, the silica-bound ZSM-5 used as the alkylation catalyst in the process of the invention provides lower xylene make, with the xylene content of

the alkylation product typically being no greater than 900 ppmw, preferably no greater than 800 ppmw. In particular, the process of the present invention can provide ethylene conversion of at least 96 wt.%, preferably at least 96.5 wt% and less than 800 ppmw xylenes/EB, preferably less than 750 ppmw xylenes/EB, after
5 4 days on stream at ethylene WHSV of 4, aromatics/ethylene ratio of 50 and inlet temperatures of 750°F. Furthermore, residue production can be limited by using the present process which can provide an ethylbenzene-rich product stream containing no greater than 0.4 wt.%, preferably no greater than 0.3, wt.% C₁₁₊ residue.

10 In one embodiment of the invention, the polyalkylating and transalkylating steps can be carried out in a single reactor preferably using the same catalyst bed by recycling polyalkylated aromatic products, e.g., a *para*-diethylbenzene-rich stream, back to the alkylating reactor. Such a procedure is especially useful wherein the ZSM-5 catalyst composite employed exhibits both alkylation and
15 transalkylation activity. Alternatively, the transalkylating step can be carried out in a transalkylating reactor separate from the alkylating reactor. In such instances each reactor may employ the same or different catalyst composites in their respective catalyst beds. A particularly preferred embodiment employs an alkylating and/or transalkylating reactor having four to six catalyst beds.

20 The following examples will serve to further illustrate processes and some advantages of the present invention.

Example 1 Preparation of ZSM-5 Catalysts

Silica Bound ZSM-5 Catalyst

25 A silica bound catalyst of the present invention was formulated by the following procedure: 178 parts of a small crystal ZSM-5 (0.02 - 0.05 micron size) drycake was added to a muller mixer along with 22 parts of a precipitated silica. The powders were mixed and then 50 parts of Ludox HS-40 colloidal silica was added along with 12 parts of a 50% caustic/water solution and 76 parts of water.
30 Mixing was done to ensure uniformity of the mull mix and then the sample was extruded through a 1/16" cylindrical die plate. The material was dried and then

ammonium nitrate exchanged to reduce the sodium level, introduced with the caustic, to less than 500 ppm. After exchange, the catalyst was nitrogen pre-calcined at 900°F for 3 hours and then air was slowly introduced and the catalyst was burned free of carbon at 1000°F for 6 hours. Steam was then introduced at
5 1000°F for 4 hours.

Alumina Bound ZSM-5 Catalyst

A comparative alumina bound catalyst was formulated by the following procedure: 250 parts of a small crystal ZSM-5 (0.02 - 0.05 micron size) drycake
10 was added to a muller mixer along with 164 parts of pseudoboehmite alumina. The powder was mixed and then 238 parts of water was added. Mixing was done to ensure uniformity of the mull mix and then the sample was extruded through a 1/16" cylindrical die plate. The material was dried and then the catalyst was nitrogen pre-calcined at 900°F for 3 hours and then air was slowly introduced and
15 the catalyst was burned free of carbon at 1000°F for 6 hours. Steam was then introduced at 1000°F for 4 hours.

Determination of Crystal Size

The crystal size of the ZSM-5 is measured to be small crystal (0.02 to 0.05
20 micron) by the use of Transmission Electron Microscopy (TEM).

Determination of Diffusion Barrier, D/r^2

By selecting appropriate probe molecules with known molecular dimensions (in the range of ~4 to 10 angstroms), it is possible to investigate
25 shapes and sizes of pore openings in molecular sieves. From among linear, branched, and cyclic paraffins, as well as substituted benzene, molecules are selected to probe small, intermediate, and large-pore zeolites. Data are collected using a TA 2950 TGA. About 30 mg are loaded into the TGA. After pretreating in helium at 500°C, the sample is cooled to sorption temperature, e.g., 120°C for
30 2,2-Dimethylbutane, and the hydrocarbon is introduced. The raw data obtained are weight vs. time. In addition to total hydrocarbon sorption capacity, uptake

rates are also obtained from the linear portion of the initial uptake vs. square root of time plot. Using the Crank equation [Crank, "The Mathematics of Diffusion", Oxford University Press, Ely House, London, 1957] for flat plate geometry, the following equation is derived for ZSM-5:

5
$$D/r^2 (x10^{-6}) = 40834.5 \times (S/Q)^2$$

where S is the slope and Q is the capacity for n-C₆. The constant is calculated by replacing the equilibrium capacity for 2,2-Dimethylbutane with the ratio of capacities of 2,2-Dimethylbutane to nC₆ for a pure material.

10

Example 2 Pilot Plant Testing

The catalyst in Example 1 was employed for the alkylation of benzene with ethylene under conditions comprising an ethylene WHSV of from 2 to 4 hr⁻¹, benzene to ethylene weight ratio of 50, pressure of 250 psig, and temperature of
15 from 730° to 780°F. The catalyst was tested in a simulation of a top catalyst bed in a 4 to 6 bed reactor.

As shown in Figure 1, catalyst stability for the silica-bound catalyst was greater than that of the comparative alumina-bound catalyst at inlet temperatures of 750°F as measured by ethylene conversion over days on stream at an ethylene
20 WHSV of 4, aromatic/ethylene weight ratio of about 50.

Xylenes make for the two catalysts were compared at operating conditions that offer stable operation, i.e., 750°F for the silica-bound catalyst and 780°F for the alumina-bound catalyst. Figure 2 shows a significant reduction in xylene make for the new catalyst.

25 Diethylbenzene (DEB) make from the alkylating reactor is the major by-product of ethylbenzene production. The DEBs are reacted with benzene to be converted back to ethylbenzene in a transalkylating reactor. Figure 3 depicts a significant increase in *para*-diethylbenzene / total DEB for the present invention at varying inlet temperatures compared to the alumina-bound catalyst. *para*-
30 Diethylbenzene is more readily converted back to ethylbenzene by

transalkylation. The catalysts are tested under comparable conditions (ethylene WHSV of 2, benzene/ethylene weight ratio of about 50 and inlet temperatures of 730-780°F for silica-bound and 750°-780°F for alumina-bound catalysts). Data are also provided for silica-bound catalyst at WHSV of 2.4.

- 5 DEB conversion for both catalysts indicated similar activity for DEB conversion as depicted in Figure 4 under comparable conditions (ethylene WHSV of 2, benzene/ethylene weight ratio of about 50 and inlet temperatures of 750°F for silica-bound and 780°F for alumina-bound catalysts). Thus the silica bound catalyst can be useful in both polyalkylating and transalkylating reactions.

CLAIMS

What we claim is:

- 5 1. A process for alkylating aromatics which comprises contacting an aromatic-containing feed with alkylating agent in the presence of a silica-bound ZSM-5 zeolite catalyst, wherein the ZSM-5 has a crystal size no greater than 0.05 micron, said contacting being conducted under alkylating conditions to provide a product containing a monoalkylated aromatic fraction and a polyalkylated
10 aromatic fraction, wherein the polyalkylated aromatic fraction contains at least 40 wt.% of the *para*-dialkylaromatic species.
2. The process of claim 1 wherein said catalyst contains at least 70 wt.% zeolite and said zeolite has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of greater than 40, and a
15 crystal size of 0.02 to 0.05 micron.
3. The process of claim 1 wherein said catalyst contains from 70-90 wt.% zeolite and said zeolite has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio ranging from about 60 to about 80.
20
4. The process of claim 1 wherein said catalyst contains 75-85 wt.% zeolite and said zeolite has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of about 70.
5. The process of claim 1 wherein said aromatic-containing feed comprises
25 benzene, said alkylating agent comprises ethylene and said *para*-dialkylaromatic is *para*-diethylbenzene.
6. The process of claim 5 wherein said alkylating conditions include a temperature of from about 650 to 900°F (343 to 482°C), a pressure of about
30 atmospheric to about 3000 psig, a WHSV based on ethylene of from about 0.5 to about 10.0 hr^{-1} and a mole ratio of benzene to ethylene of from 1:1 to 30:1.

7. The process of claim 5 which provides ethylene conversion of at least 96 wt.% ethylene conversion after 4 days on stream at ethylene WHSV of 4, aromatics/ethylene ratio of 50 and inlet temperature of 750°F; and makes *para*-diethylbenzene/total diethylbenzene greater than 45 wt.% at ethylene WHSV of 2, aromatics/ethylene ratio of 50 and inlet temperature of 750°F.

8. The process of claim 1 wherein said catalyst has a Diffusion Parameter, D/r^2 , for 2,2-dimethylbutane of at least 500, when measured at a temperature of 120°C and a 2,2-dimethylbutane pressure of 60 torr (8 kPa).

9. The process of claim 1 wherein said catalyst has a Diffusion Parameter, D/r^2 , for 2,2-dimethylbutane of at least 700 to 2000, when measured at a temperature of 120°C and a 2,2-dimethylbutane pressure of 60 torr (8 kPa).

15

10. A process for preparing a monoalkylated aromatic compound which comprises:

- i) contacting an aromatic-containing feed in an alkylating reactor with alkylating agent in the presence of a silica-bound ZSM-5 zeolite alkylation catalyst, wherein the ZSM-5 has a crystal size no greater than 0.05 micron, said contacting being conducted under alkylating conditions to provide a product containing a monoalkylated aromatic fraction and a polyalkylated aromatic fraction, wherein the polyalkylated aromatic fraction contains at least 40 wt% of the *para*-dialkylaromatic species;
- 25 ii) separating the polyalkylated aromatic fraction from the product, and
- iii) contacting the polyalkylated aromatic fraction in the presence of unsubstituted aromatic and a transalkylation catalyst under transalkylating conditions to provide a mono-alkylated aromatic-rich stream.

11. The process of claim 10 wherein said alkylation catalyst contains at least 70 wt.% zeolite and said zeolite has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio ranging from 60 to 80 and a crystal size of 0.02 to 0.05 micron.

5 12. The process of claim 10 wherein step iii) is carried out in a transalkylating reactor separate from said alkylating reactor.

13. The process of claim 10 wherein step iii) is carried out by recycling said *para*-dialkylaromatic-rich stream to said alkylating reactor.

10

14. The process of claim 10 wherein said transalkylation catalyst is a silica-bound ZSM-5 zeolite catalyst composite having a crystal size no greater than 0.05 micron.

15 15. The process of claim 10 wherein said mono-alkylated aromatic comprises ethylbenzene, said aromatic-containing feed comprises benzene, said alkylating agent comprises ethylene and said *para*-dialkylaromatic is *para*-diethylbenzene.

16. The process of claim 15 wherein said alkylating conditions include a
20 temperature of from about 650 to 900°F (343 to 482°C), a pressure of about atmospheric to about 3000 psig, a WHSV based on ethylene of from about 0.5 to about 2.0 hr⁻¹ and a mole ratio of benzene to ethylene of from 1:1 to 30:1

17. The process of claim 15 which provides ethylene conversion of at least 96
25 wt.%, and less than 800 ppm xylenes/EB, after 4 days on stream at ethylene WHSV of 4, aromatics/ethylene ratio of 50 and inlet temperature of 750°F; and provides *para*-diethylbenzene/total diethylbenzene at greater than 45 wt.% at ethylene WHSV of 2 aromatics/ethylene ratio of 50 and inlet temperature of 750°F.

30

18. The process of claim 15 wherein said ethylbenzene-rich stream contains no greater than 0.6 wt% of C₁₁₊ residue.
19. The process of claim 11 wherein said catalyst has a Diffusion Parameter, D/r^2 , for 2,2-dimethylbutane of at least 500, when measured at a temperature of 120°C and a 2,2-dimethylbutane pressure of 60 torr (8 kPa).
- 5

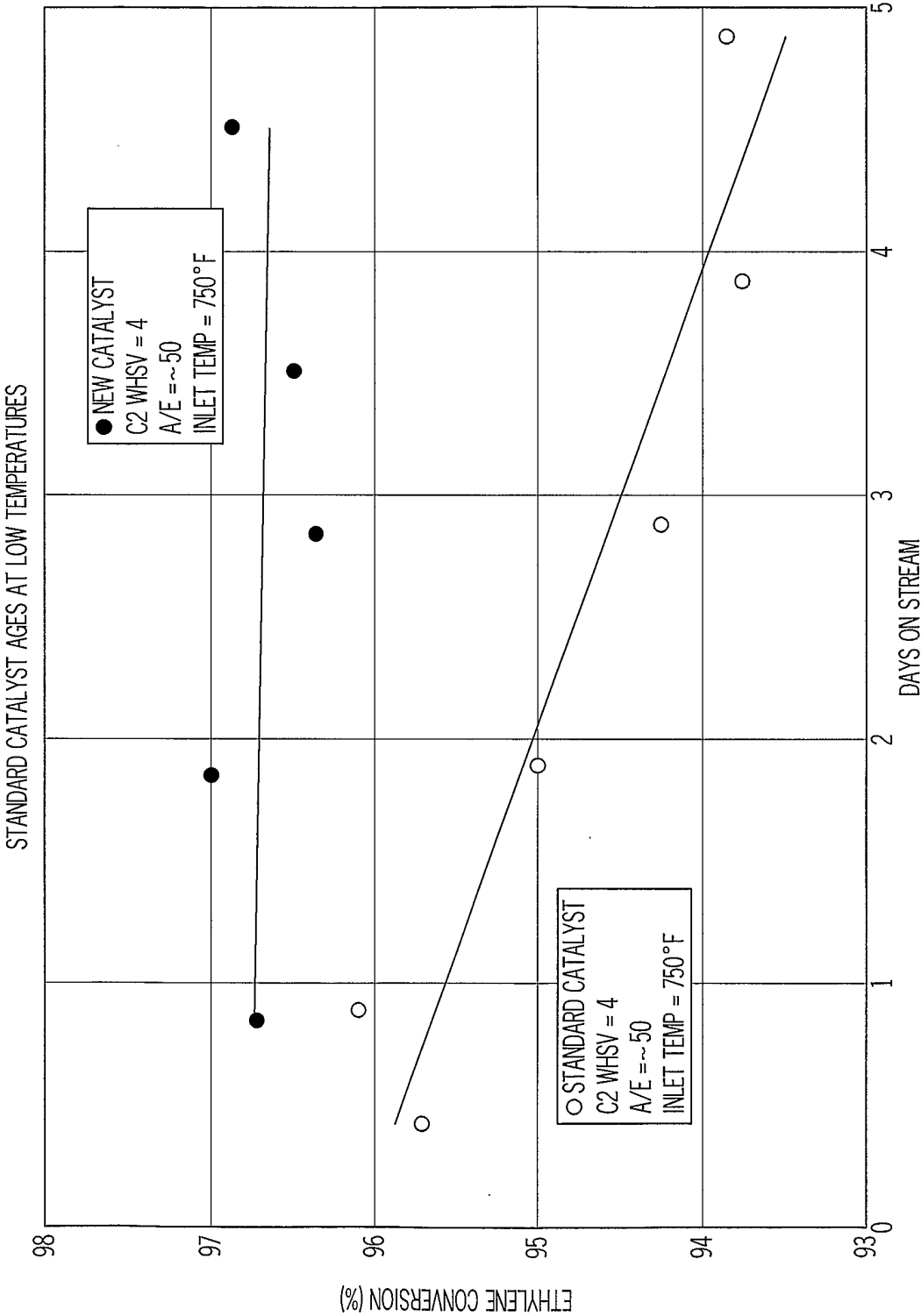


FIG. 1

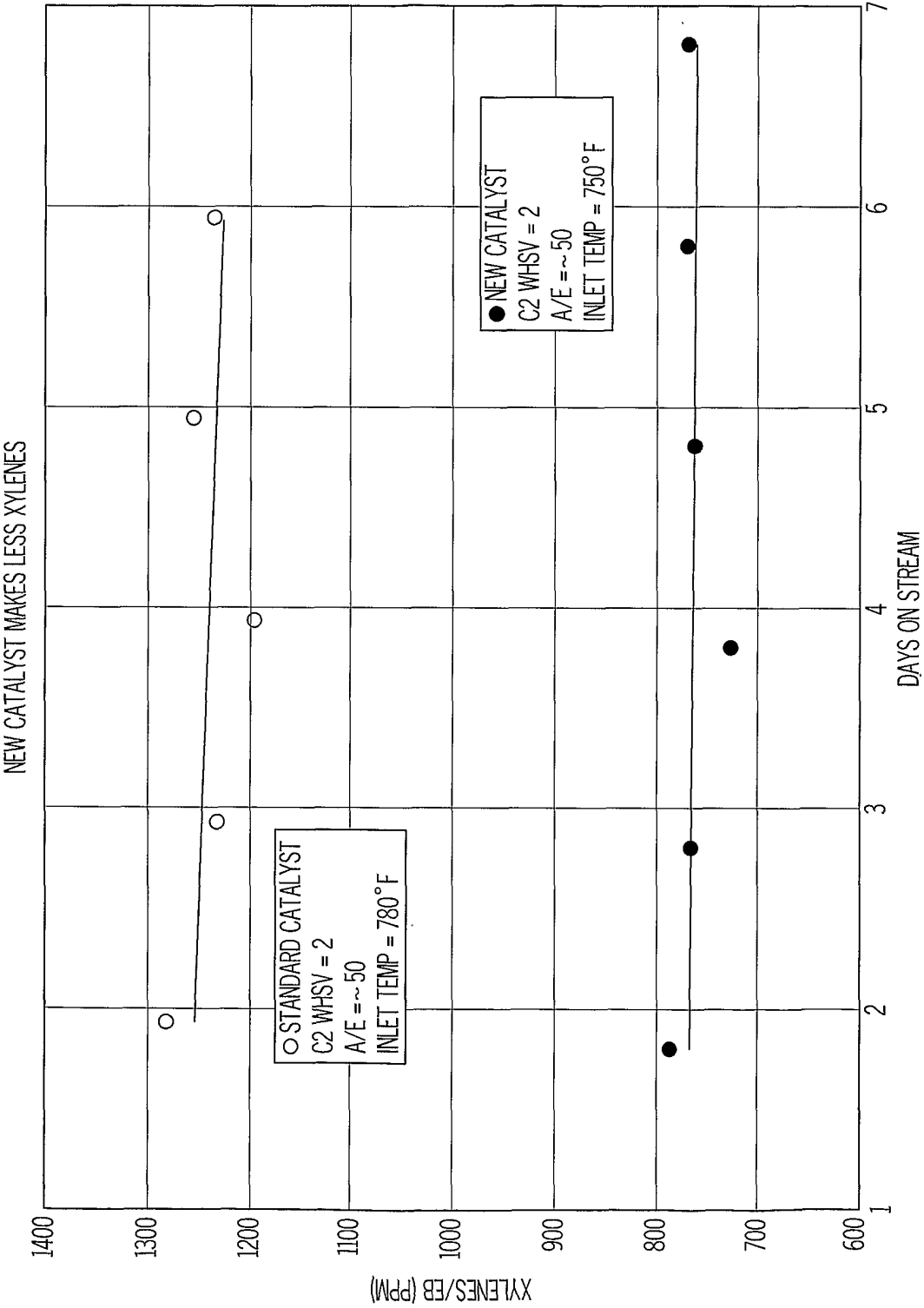


FIG. 2

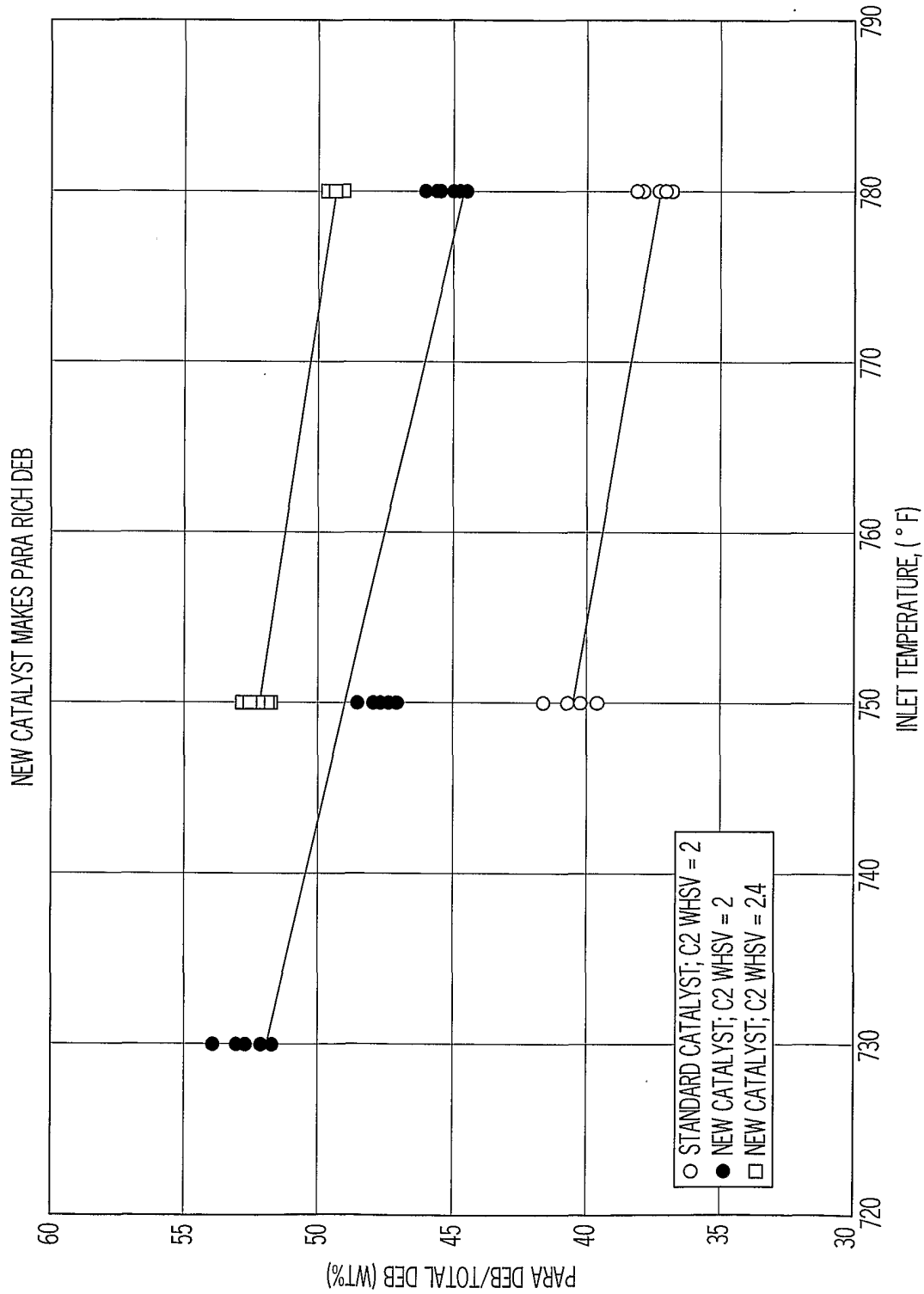


FIG. 3

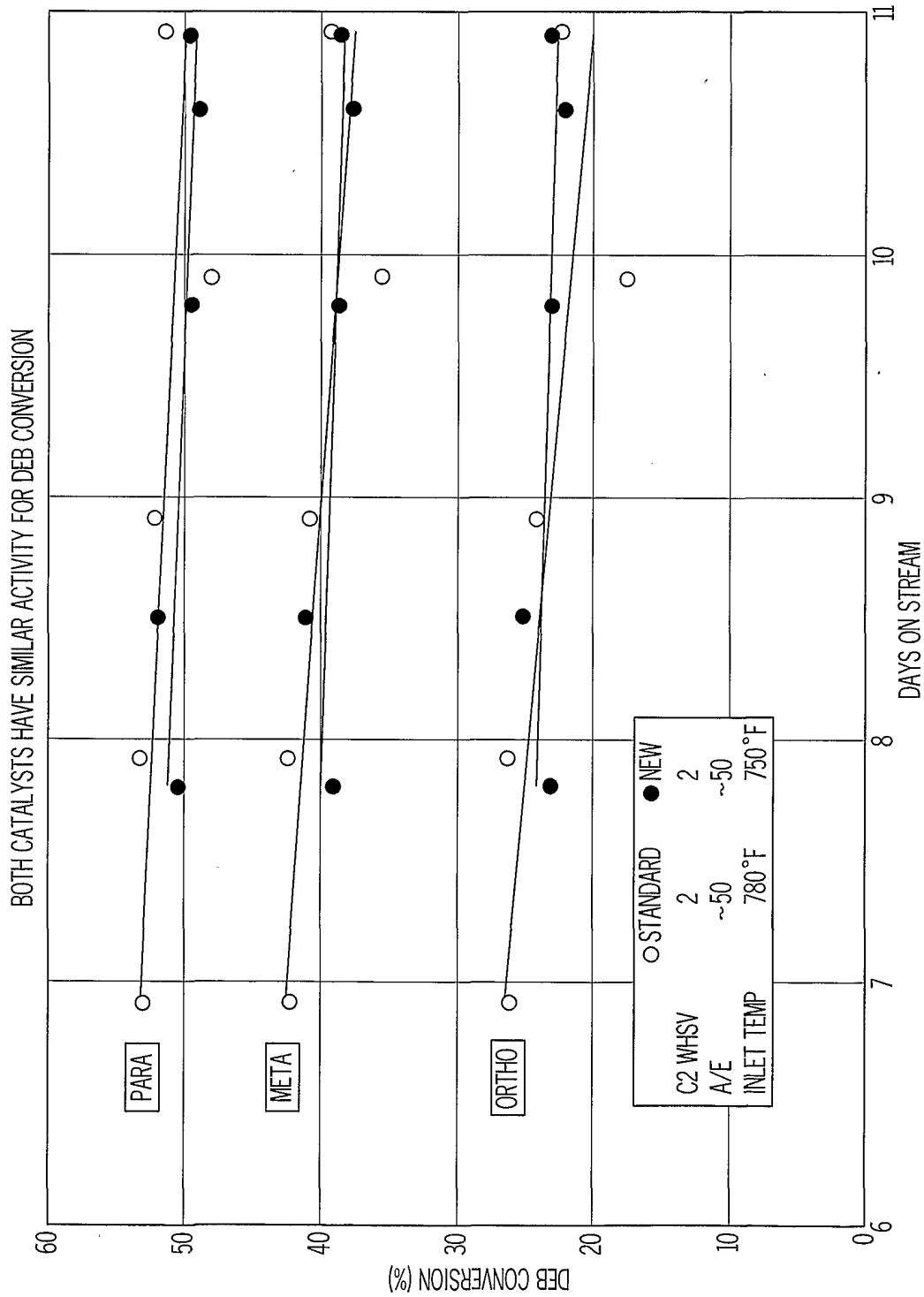


FIG. 4

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/26201

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C2/66 C07C15/073

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 157 185 A (CHU ET AL) 20 October 1992 (1992-10-20) column 10; claims	1-9
Y	column 10; claims	10-19
Y	WO 95 01318 A (MOBIL OIL CORPORATION) 12 January 1995 (1995-01-12) claims	10-19



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

° Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

28 November 2001

Date of mailing of the international search report

06/12/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Van Geyt, J

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1 to 19 (all in part)

1. Present claims 1 and 10 relate to an extremely large number of possible starting compounds. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the starting compounds claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the reaction of the alkylatable compounds listed on 7, lines 12 to 17, with the alkylating agents listed on page 8, lines 15 to 21.

2. Present claims 1, 7, 10, 17 and 18 relate to a product defined by reference to a desirable characteristic or property, namely the concentration of para-dialkyl compounds in the product (claims 1, 7, 10 and 17) or the concentration of residue in the product (claim 18). The claims cover all products having this characteristic or property, whereas the application provides support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT for only a very limited number of such products. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Independent of the above reasoning, the claims also lack clarity (Article 6 PCT). An attempt is made to define the product by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible. Consequently, the search has been carried out for those parts of the claims which appear to be clear, supported and disclosed, namely those parts relating to the products prepared according to the reaction conditions given in the claims.

3.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/26201

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5157185	A	20-10-1992	NONE	
WO 9501318	A	12-01-1995	AU 7062094 A WO 9501318 A1	24-01-1995 12-01-1995