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CA 2875668 A1 2013/12/12

(21) 2 875 668

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(86) Date de dépôt PCT/PCT Filing Date: 2013/06/17
(87) Date publication PCT/PCT Publication Date: 2013/12/12
(85) Entrée phase nationale/National Entry: 2014/12/03
(86) N° demande PCT/PCT Application No.: US 2013/046077
(87) N° publication PCT/PCT Publication No.: 2013/185149
(30) Priorités/Priorities: 2012/06/05 (US61/655,605); 2012/09/27 (US13/628,258)

(51) Cl.Int./Int.Cl. *C07C 1/247* (2006.01)

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(54) Titre : PROCEDE DE CONVERSION D'UNE MATIERE HYDROCARBONEE EN UN PRODUIT HYDROCARBONE FLUIDE COMPRENANT DU P-XYLENE

(54) Title: METHOD FOR CONVERTING A HYDROCARBONACEOUS MATERIAL TO A FLUID HYDROCARBON PRODUCT COMPRISING P-XYLENE

(57) Abrégé/Abstract:
The invention relates to a method for producing a fluid hydrocarbon product, and more specifically, to a method for producing a fluid hydrocarbon product via catalytic pyrolysis. The reactants comprise hydrocarbonaceous materials (e.g., biomass). The catalyst comprises a zeolite catalyst treated with a silicone compound. The product comprises p-xylene.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 December 2013 (12.12.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/185149 A1

(51) International Patent Classification:
C07C 1/247 (2006.01)

(21) International Application Number:
PCT/US2013/046077

(22) International Filing Date:
17 June 2013 (17.06.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/655,605 5 June 2012 (05.06.2012) US
13/628,258 27 September 2012 (27.09.2012) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

— *with information concerning request for restoration of the right of priority in respect of one or more priority claims (Rules 26bis.3 and 48.2(b)(vii))*

WO 2013/185149 A1

(54) **Title**: METHOD FOR CONVERTING A HYDROCARBONACEOUS MATERIAL TO A FLUID HYDROCARBON PRODUCT COMPRISING P-XYLENE

(57) **Abstract**: The invention relates to a method for producing a fluid hydrocarbon product, and more specifically, to a method for producing a fluid hydrocarbon product via catalytic pyrolysis. The reactants comprise hydrocarbonaceous materials (e.g., biomass). The catalyst comprises a zeolite catalyst treated with a silicone compound. The product comprises p-xylene.

METHOD FOR CONVERTING A HYDROCARBONACEOUS MATERIAL TO A FLUID HYDROCARBON PRODUCT COMPRISING P-XYLENE

This application claims priority under 35 U.S.C. §119(e) to U.S. Provisional Application Serial No. 61/655,605 filed June 5, 2012. The disclosure in this provisional application is incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT.

The U.S. Government has a paid-up license in this invention and the right in limited circumstances to require the patent owner to license others on reasonable terms as provided for by the terms of Grant No. CBET-0747996 awarded by the National Science Foundation.

FIELD OF INVENTION

This invention relates to a method for converting a hydrocarbonaceous material to a fluid hydrocarbon product comprising p-xylene, and more specifically, to a method for converting a hydrocarbonaceous material to a fluid hydrocarbon product comprising p-xylene via catalytic pyrolysis.

BACKGROUND

p-Xylene is used as a starting material for plasticizers and polyester fibers. The oxidation of p-xylene is used to commercially synthesize terephthalic acid. Further esterification of the acid with methanol forms dimethyl terephthalate. Both monomers may be used in the production of polyethylene terephthalate (PET) plastic bottles and polyester clothing.

SUMMARY

Catalytic pyrolysis, including catalytic fast pyrolysis (CFP), is a process that may be used to convert a hydrocarbonaceous material (e.g., biomass) into a fluid hydrocarbon product using rapid heating rates in the presence of a catalyst. With the inventive

method, the fluid hydrocarbon product comprises p-xylene, and may further comprise additional aromatics, olefins, and the like.

With this invention, a hydrocarbonaceous material may be fed to a reactor (e.g., a fluidized-bed reactor) where the hydrocarbonaceous material may first thermally decompose to form one or more pyrolysis products. The pyrolysis products may comprise one or more pyrolysis vapors. These pyrolysis products may react in the presence of a modified zeolite catalyst to form one or more aromatic compounds as well as olefin compounds, CO and CO_2. The modified zeolite catalyst may comprise pores with pore mouth openings that have been reduced in size. The pyrolysis products may enter the pores in the modified zeolite catalyst where they may undergo reaction. The products formed in the catalyst pores may then diffuse out of the pores. The aromatic compounds may comprise p-xylene or xylenes with a relatively high selectivity towards p-xylene. Advantages of this process include: 1) all the desired chemistry may occur in a single-step process, 2) the process may use a relatively inexpensive zeolite catalyst, and 3) p-xylene may be produced at a relatively high level of production.

p-Xylene may be the most valuable of the xylenes (i.e., o-, m- and p-xylenes). However, during the catalytic pyrolysis of various hydrocarbonaceous materials, the xylenes may be formed with the *m*-xylene selectivity and/or o-xylene selectivity being the same as or higher than the *p*-xylene selectivity. The p-xylene that is produced may also isomerize to m-xylene and/or o-xylene. As a result, xylenes with undesirably high selectivities to m-xylene and/or o-xylene may be formed. The problem therefore is to provide a method that allows for the production of p-xylene or xylenes with a relatively high selectivity to p-xylene. This invention provides a solution to this problem. The present invention provides for the use of a zeolite catalyst that has been modified to improve selectivity towards p-xylene. The zeolite catalyst may comprise catalytic sites on the external surface of the catalyst and pores with pore mouth openings. The pores may contain internal catalytic sites, some of which may be positioned near the pore mouth openings, and some of which may be internal catalytic sites positioned away from the pore mouth openings. The catalyst may be modified by treating it with an effective amount of a silicone compound to reduce the size of the pore mouth openings and to render at least some of the catalytic sites on the external surfaces of the catalyst inaccessible to the reactants. The treatment process may also be used to render at least

some of the catalytic sites in the pores near the pore mouth openings inaccessible to the reactants.

The zeolite catalyst may be treated by applying a silicone compound to the surface of the catalyst. Application of the silicone compound may reduce the size of the pore mouth openings in the catalyst as well as cover or obscure catalytic sites on the external surface of the catalyst as well as inside the pores of the catalyst near the pore mouth openings. The covering of the catalytic sites with the treatment layer may inhibit and/or extinguish their catalytic activity. Catalytic sites on the external surface of the catalyst as well as catalytic sites in the pores near the pore mouth openings are believed to be unselective in the production of xylenes, while the catalytic sites in the pores away from the pore mouth openings appear to provide for an increase in para selectivity. Inhibition or extinction of the activity of the catalytic sites on the external surface of the catalyst and in the pores of the catalyst near the pore mouth openings may increase the proportion of the catalytic reaction that occurs within the zeolite pores away from the pore mouth openings, hence an increase in selectivity to p-xylene.

The pores with pore mouth openings that have been reduced in size may allow for an increase in *para* selectivity for the xylenes. This may be due to the fact that the reduced pore mouth openings may allow p-xylene to diffuse out of the pores while the diffusion of m-xylene and o-xylene may be restricted. This is illustrated in Fig. 2. In Fig. 2, a zeolite catalyst is shown that has a pore mouth opening that has been reduced in size to allow p-xylene, but not m- or o-xylene, to diffuse out of the zeolite pore.

This invention relates to a method for producing a fluid hydrocarbon product comprising p-xylene from a hydrocarbonaceous material, comprising: feeding the hydrocarbonaceous material to a reactor; pyrolyzing within the reactor at least a portion of the hydrocarbonaceous material under reaction conditions sufficient to produce a pyrolysis product; and catalytically reacting at least a portion of the pyrolysis product under reaction conditions in the presence of a zeolite catalyst to produce the fluid hydrocarbon product; the zeolite catalyst comprising pores with pore mouth openings and catalytic sites on the external surface of the catalyst, and an effective amount of a treatment layer derived from a silicone compound to reduce the size of the pore mouth openings and to render at least some of the catalytic sites on the external surface of the catalyst inaccessible to the pyrolysis product. Catalytic sites may be positioned in the

pores near the pore mouth openings and the treatment layer may render at least some of these catalytic sites inaccessible to the pyrolysis product.

With the present invention, the selectivity to p-xylene in the xylenes may be up to 100% when the only active catalytic sites are within the catalyst pores, and the only xylene to diffuse from the catalyst pores is p-xylene. In an embodiment, p-xylene may be produced in preference to o-xylene and/or m-xylene, but some o-xylene and/or m-xylene may nevertheless be produced.

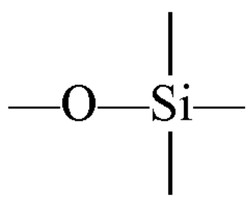
With the present invention, the fluid hydrocarbon product produced using the foregoing method may comprise xylenes and may be characterized by a p-xylene selectivity in the xylenes of at least about 40%, or at least about 45%, or at least about 50%, or at least about 55%, or at least about 60%, or at least about 65%, or at least about 70%, or at least about 75%, or at least about 80%, or at least about 85%, or at least about 90%.

The zeolite catalyst may be treated with the silicone compound to reduce the size of the pore openings, and cover or obscure catalytic sites on the external surface of the catalyst. This treatment process may also be used to cover or obscure catalytic sites in the pores near the pore mouths openings. The catalytic sites may also be referred to as acid sites. The covered or obscured catalytic sites may be referred to as deactivated catalytic sites. The silicone compound may have a molecular size that is incapable of entering the pores of the catalyst. During the catalyst treatment process, the silicone compound may be applied to the catalyst and subsequently calcined. This process may be repeated until the desired level of treatment is provided. The fraction of catalytic sites on the external surface of the catalyst that may be deactivated by treatment with the silicone compound may be at least about 15%, or at least about 25%, or at least about 35%, or at least about 45%, or at least about 55%, or at least about 65%, or at least about 75%, or at least about 85%, or at least about 90%, or at least about 95%, or at least about 98%, or at least about 99%, of the available catalytic sites. The fraction of catalytic sites in the pores of the catalyst near the pore mouth openings that may be deactivated by treatment with the silicone compound may be at least about 20%, or at least about 25%, or at least about 30%, or at least about 33%, or at least about 35%, or at least about 40%, or at least about 45%, or at least about 49%, or at least about 50%, or at least about 55%, or at least about 60%, or at least about 65%, or at least about 70%, or at least about 75%,

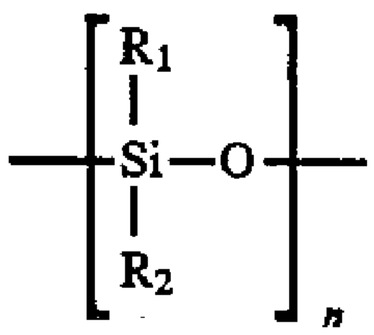
or at least about 80%, or at least about 85%, or at least about 90%, or at least about 95% , or at least about 99% of the available catalytic sites. The average diameter of the pore mouth openings subsequent to treatment with the silicone compound may be in the range from about 5 to about 10 angstroms, or from about 5.2 to about 7.4 angstroms.

The zeolite catalyst may comprise silica and alumina. The silica to alumina molar ratio may be in the range from about 10:1 to about 50:1, or in the range from about 10:1 to about 40:1, or in the range from about 10:1 to about 20:1, or about 15:1. The zeolite catalyst may further comprise nickel, platinum, vanadium, palladium, manganese, cobalt, zinc, copper, chromium, gallium, an oxide of one or more thereof, or a mixture of two or more thereof.

The silicone compound may comprise a compound containing at least one group represented by the formula



The silicone compound may be represented by the formula:



wherein R_1 and R_2 independently comprise hydrogen, halogen, hydroxyl, alkyl, alkoxyl, halogenated alkyl, aryl, halogenated aryl, aralkyl, halogenated aralkyl, alkaryl or halogenated alkaryl; and n is a number that is at least 2. R_1 and/or R_2 may comprise methyl, ethyl or phenyl. n may be a number in the range from about 3 to about 1000.

The silicone compound may have a number average molecular weight in the range from about 80 to about 20,000, or from about 150 to 10,000.

The silicone compound may comprise dimethylsilicone, diethylsilicone, phenylmethylsilicone, methylhydrogensilicone, ethylhydrogen silicone, phenylhydrogen silicone, methylethyl silicone, phenylethyl silicone, diphenyl silicone, methyltrifluoropropyl silicone, ethyltrifluoropropyl silicone, polydimethyl silicone,

tetrachloro-phenylmethyl silicone, tetrachlorophenylethyl silicone, tetrachlorophenylhydrogen silicone, tetrachlorophenylphenyl silicone, methylvinyl silicone, hexamethyl cyclotrisiloxane, octamethyl cyclotetrasiloxane, hexaphenyl cyclotrisiloxane, octaphenyl cyclotetrasiloxane, or a mixture of two or more thereof.

The silicone compound may comprise a tetraorthosilicate. The silicone compound may comprise tetramethylorthosilicate, tetraethylorthosilicate, or a mixture thereof.

The reactor may comprise a continuously stirred tank reactor, a batch reactor, a semi-batch reactor, a fixed bed reactor or a fluidized bed reactor. Fluidized bed reactors may be particularly advantageous.

The hydrocarbonaceous material may comprise a solid hydrocarbonaceous material, a semi-solid hydrocarbonaceous material, a liquid hydrocarbonaceous material, or a mixture of two or more thereof. The hydrocarbonaceous material may comprise biomass. The hydrocarbonaceous material may comprise plastic waste, recycled plastics, agricultural solid waste, municipal solid waste, food waste, animal waste, carbohydrates, lignocellulosic materials, xylitol, glucose, cellobiose, hemi-cellulose, lignin, sugar cane bagasse, glucose, wood, corn stover, or a mixture of two or more thereof. The hydrocarbonaceous material may comprise furan and/or 2-methylfuran. The hydrocarbonaceous material may comprise pinewood. The hydrocarbonaceous material may comprise pyrolysis oil derived from biomass, a carbohydrate derived from biomass, an alcohol derived from biomass, a biomass extract, a pretreated biomass, a digested biomass product, or a mixture of two or more thereof. Mixtures of two or more of any of the foregoing may be used as the hydrocarbonaceous feed material.

The reactor may be operated at a temperature in the range from about 400°C to about 600°C, or from about 425 °C to about 500 °C, or from about 440 °C to about 460°C.

The hydrocarbonaceous material may be fed to the reactor at a mass normalized space velocity of up to about 3 $hour^{-1}$, or up to about 2 $hour^{-1}$, or up to about 1.5 $hour^{-1}$, or up to about 0.9 $hour^{-1}$, or in the range from about 0.01 $hour^{-1}$ to about 3 $hour^{-1}$, or in the range from about 0.01 to about 2 $hour^{-1}$, or in the range from about 0.01 to about 1.5 $hour^{-1}$, or in the range from about 0.01 to about 0.9 $hour^{-1}$, or in the range from about

0.01 hour^{-1} to about 0.5 hour^{-1}, or in the range from about 0.1 hour^{-1} to about 0.9 hour^{-1}, or in the range from about 0.1 hour^{-1} to about 0.5 hour^{-1}.

The reactor may be operated at a pressure of at least about 100 kPa, or at least about 200 kPa, or at least about 300 kPa, or at least about 400 kPa. The reactor may be operated at a pressure below about 600 kPa, or below about 400 kPa, or below about 200 kPa. The reactor may be operated at a pressure in the range from about 100 to about 600 kPa, or in the range from about 100 to about 400 kPa, or in the range from about 100 to about 200 kPa.

The method may be conducted under reaction conditions that minimize coke production. The pyrolysis product may be formed with less than about 30 wt%, or less than about 25 wt%, or less than about 20 wt%, or less than about 15 wt%, or less than about 10 wt%, of the pyrolysis product being coke.

The method may further comprise the step of recovering the fluid hydrocarbon product. The fluid hydrocarbon product may further comprise, in addition to p-xylene, other aromatic compounds and/or olefin compounds. The fluid hydrocarbon product may further comprise benzene, toluene, ethylbenzene, methylethylbenzene, trimethylbenzene, o-xylene, m-xylene, indanes naphthalene, methylnaphthelene, dimethylnaphthalene, ethylnaphthalene, hydrindene, methylhydrindene, dimethylhydrindene, or a mixture of two or more thereof.

The carbon yield of aromatics in the fluid hydrocarbon product may be at least about 10%, or at least about 15%, or at least about 22%. The carbon yield of olefins in the fluid hydrocarbon product may be at least about 3%, or at least about 6%, or at least about 9%, or at least about 12 %. The mass yield of p-xylene may be at least about 1.5 wt%, or at least about 2 wt%, or at least about 2.5 wt%, or at least about 3 wt%.

The catalytically reacting step may comprise a dehydration, decarbonylation, decarboxylation, isomerization, oligomerization and/or dehydrogenation reaction.

The pyrolyzing step and the catalytically reacting steps may be carried out in a single vessel. Alternatively, the pyrolyzing step and the catalytically reacting steps may be carried out in separate vessels.

Other advantages and novel features of the present invention will become apparent from the following detailed description of various non-limiting embodiments of the invention when considered in conjunction with the accompanying figures. In cases

where the present specification and a document incorporated by reference include conflicting and/or inconsistent disclosure, the present specification shall control.

BRIEF DESCRIPTION OF THE DRAWINGS

Non-limiting embodiments of this invention will be described by way of example with reference to the accompanying figures, which are schematic and are not intended to be drawn to scale. In the figures, each identical or nearly identical component illustrated is typically represented by a single numeral. For purposes of clarity, not every component is labeled in every figure, nor is every component of each embodiment of the invention shown where illustration is not necessary to allow those of ordinary skill in the art to understand the invention. In the figures:

FIGS. 1A and 1B are schematic illustrations of a CFP process for converting a solid hydrocarbonaceous material to a fluid hydrocarbon product.

FIG. 2 is a schematic illustration showing a pore with a pore mouth opening that has been reduced in size and the diffusion of p-xylene out of the pore.

DETAILED DESCRIPTION

All ranges and ratio limits disclosed in the specification and claims may be combined in any manner. It is to be understood that unless specifically stated otherwise, references to "a," "an," and/or "the" may include one or more than one, and that reference to an item in the singular may also include the item in the plural.

The phrase "and/or" should be understood to mean "either or both" of the elements so conjoined, i.e., elements that are conjunctively present in some cases and disjunctively present in other cases. Other elements may optionally be present other than the elements specifically identified by the "and/or" clause, whether related or unrelated to those elements specifically identified unless clearly indicated to the contrary. Thus, as a non-limiting example, a reference to "A and/or B," when used in conjunction with open-ended language such as "comprising" can refer, in one embodiment, to A without B (optionally including elements other than B); in another embodiment, to B without A (optionally including elements other than A); in yet another embodiment, to both A and B (optionally including other elements); etc.

The word "or" should be understood to have the same meaning as "and/or" as defined above. For example, when separating items in a list, "or" or "and/or" shall be interpreted as being inclusive, i.e., the inclusion of at least one, but also including more than one, of a number or list of elements, and, optionally, additional unlisted items. Only terms clearly indicated to the contrary, such as "only one of" or "exactly one of," or may refer to the inclusion of exactly one element of a number or list of elements. In general, the term "or" as used herein shall only be interpreted as indicating exclusive alternatives (i.e. "one or the other but not both") when preceded by terms of exclusivity, such as "either," "one of," "only one of," or "exactly one of."

The phrase "at least one," in reference to a list of one or more elements, should be understood to mean at least one element selected from any one or more of the elements in the list of elements, but not necessarily including at least one of each and every element specifically listed within the list of elements and not excluding any combinations of elements in the list of elements. This definition also allows that elements may optionally be present other than the elements specifically identified within the list of elements to which the phrase "at least one" refers, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, "at least one of A and B" (or, equivalently, "at least one of A or B," or, equivalently "at least one of A and/or B") can refer, in one embodiment, to at least one, optionally including more than one, A, with no B present (and optionally including elements other than B); in another embodiment, to at least one, optionally including more than one, B, with no A present (and optionally including elements other than A); in yet another embodiment, to at least one, optionally including more than one, A, and at least one, optionally including more than one, B (and optionally including other elements); etc.

The transitional words or phrases, such as "comprising," "including," "carrying," "having," "containing," "involving," "holding," and the like, are to be understood to be open-ended, i.e., to mean including but not limited to.

The terms "pyrolysis" and "pyrolyzing" refer to the transformation of a material (e.g., a solid hydrocarbonaceous material) into one or more other materials (e.g., volatile organic compounds, gases, coke, etc.) by heat, without oxygen or other oxidants or without significant amounts of oxygen or other oxidants, and with or without the use of a catalyst.

The term "catalytic pyrolysis" refers to pyrolysis performed in the presence of a catalyst.

The terms "aromatics" or "aromatic compound" refer to a hydrocarbon compound or compounds comprising one or more aromatic groups such as, for example, single aromatic ring systems (e.g., benzyl, phenyl, etc.) and/or fused polycyclic aromatic ring systems (e.g. naphthyl, 1,2,3,4-tetrahydronaphthyl, etc.). Examples of aromatic compounds include, but are not limited to, benzene, toluene, indane, indene, 2-ethyl toluene, 3-ethyl toluene, 4-ethyl toluene, trimethyl benzene (e.g., 1,3,5-trimethyl benzene, 1,2,4-trimethyl benzene, 1,2,3-trimethyl benzene, etc.), ethylbenzene, styrene, cumene, methylbenzene, propylbenzene, xylenes (e.g., p-xylene, m-xylene, o-xylene, etc.), naphthalene, methyl-naphthalene (e.g., 1-methyl naphthalene, anthracene, 9.10-dimethylanthracene, pyrene, phenanthrene, dimethyl-naphthalene (e.g., 1,5-dimethylnaphthalene, 1,6-dimethylnaphthalene, 2,5-dimethylnaphthalene, etc.), ethyl-naphthalene, hydrindene, methyl-hydrindene, and dymethyl-hydrindene. Single ring and/or higher ring aromatics may be produced in some embodiments.

The term "petrochemicals" is used herein to refer to chemicals, chemical precursors, chemical intermediates, and the like, traditionally derived from petroleum sources. Petrochemicals include paraffins, olefins, aromatic compounds, and the like. For purposes of this application, when these materials are derived from biomass, as well as other non-petroleum sources (e.g., recycled plastics, municipal solid waste, sugar cane bagasse, wood, etc.), the term petrochemicals may be employed despite the fact that the chemicals, chemical precursors, chemical intermediates, and the like, may not be derived directly from petroleum.

The term "biomass" refers to living and recently dead biological material. In accordance with the inventive method, biomass may be converted, for example, to liquid fuel (e.g., biofuel or biodiesel) or to other fluid hydrocarbon products. Biomass may include trees (e.g., wood) as well as other vegetation; agricultural products and agricultural waste (e.g., corn stover, bagasse, fruit, garbage, silage, etc.); energy crops (e.g. switchgrass, miscanthus); algae and other marine plants; metabolic wastes (e.g., manure, sewage); and cellulosic urban waste. Biomass may be considered as comprising material that recently participated in the carbon cycle so that the release of carbon in a combustion process may result in no net increase averaged over a reasonably short

period of time. For this reason, peat, lignite, coal, shale oil or petroleum may not be considered as being biomass as they contain carbon that may not have participated in the carbon cycle for a long time and, as such, their combustion may result in a net increase in atmospheric carbon dioxide. The term biomass may refer to plant matter grown for use as biofuel, but may also includes plant or animal matter used for production of fibers, chemicals, heat, and the like. Biomass may also include biodegradable waste or byproducts that can be burnt as fuel or converted to chemicals. These may include municipal waste, green waste (the biodegradable waste comprised of garden or park waste such as grass or flower cuttings, hedge trimmings, and the like), byproducts of farming including animal manures, food processing wastes, sewage sludge, black liquor from wood pulp or algae, and the like. Biomass may be derived from plants, including miscanthus, spurge, sunflower, switchgrass, hemp, corn (maize), poplar, willow, sugarcane, and oil palm (palm oil), and the like. Biomass may be derived from roots, stems, leaves, seed husks, fruits, and the like. The particular plant or other biomass source used may not be important to the fluid hydrocarbon product produced in accordance with the inventive method, although the processing of the biomass may vary according to the needs of the reactor and the form of the biomass.

The hydrocarbonaceous feed material for the inventive method may comprise a solid hydrocarbonaceous material, a semi-solid hydrocarbonaceous material, a liquid hydrocarbonaceous material, or a mixture of two or more thereof. The solids content of the hydrocarbonaceous feed may be up to about 100% by weight, or from about 30% to about 100% by weight, or from about 50% to about 100%, or from about 70% to about 100%, or from 90% to about 100%, or from about 95% to about 100%, or from about 98% to about 100%, or from about 30% to about 95%, or from about 50% to about 95%, or from about 70% to about 95%, or from about 80% to about 95%, or from about 85% to about 95%, or from about 90% to about 95% by weight. The hydrocarbonaceous material may comprise biomass. The hydrocarbonaceous material may comprise plastic waste, recycled plastics, agricultural solid waste, municipal solid waste, food waste, animal waste, carbohydrates, lignocellulosic materials, xylitol, glucose, cellobiose, hemi-cellulose, lignin, sugar cane bagasse, glucose, wood, corn stover, or a mixture of two or more thereof. The hydrocarbonaceous material may comprise furan and/or 2-methylfuran. The hydrocarbonaceous material may comprise pinewood. The hydrocarbonaceous material

may comprise pyrolysis oil derived from biomass, a carbohydrate derived from biomass, an alcohol derived from biomass, a biomass extract, a pretreated biomass, a digested biomass product, or a mixture of two or more thereof. Mixtures of two or more of any of the foregoing may be used.

The inventive method may comprise feeding the hydrocarbonaceous material to a reactor. At least a portion of the hydrocarbonaceous material may be pyrolyzed in the reactor under reaction conditions sufficient to produce one or more pyrolysis products. At least a portion of the pyrolysis products may be catalytically reacted under sufficient conditions to produce the fluid hydrocarbon product. The reactor may comprise a continuously stirred tank reactor, a batch reactor, a semi-batch reactor, a fixed bed reactor, or a fluidized bed reactor. Advantageously, the reactor may comprise a fluidized bed reactor. The catalytic reaction step may be achieved by co-feeding the catalyst with the hydrocarbonaceous material. The catalyst may be fed separately. Part of the catalyst may be fed with the hydrocarbonaceous feed material and part of the catalyst may be fed separately.

The inventive method may be used for the production of fluid (e.g., a liquid, a supercritical fluid, and/or a gas) hydrocarbon products via a catalytic pyrolysis process (e.g., a CFP process). The fluid hydrocarbon product, or a portion thereof, may comprise a liquid at standard ambient temperature and pressure (SATP - i.e. 25°C and 100 kPa absolute pressure). The hycrocarbonaceous feed material may be pyrolyzed at intermediate temperatures (for example, in the range from about 400 °C and about 600 °C), compared to temperatures typically used in the prior art. The pyrolysis step may be conducted for an effective amount of time to produce discrete, identifiable fluid hydrocarbon products. The inventive method may involve heating the hydrocarbonaceous material (and optionally the catalyst) to the reaction temperature at relatively high heating rates (e.g., greater than about 50°C per second).

The inventive method may involve the use of specialized catalysts. These catalysts are zeolite catalysts which contain silica and alumina. The catalyst may be characterized by pores with pore mouth openings wherein the pore mouth openings have been reduced in size, and catalytic sites on the external surface of the catalyst that have been covered or obscured. The catalyst may have catalytic sites in the pores near the pore mouth openings that have been covered or obscured. The catalyst may be

treated with a silicone compound to reduce the size of the pore mouth openings and cover or obscure catalytic sites on the external surface of the catalyst and in the pores of the catalyst near the pore mouth openings. The catalyst may comprise relatively small particles, which may be agglomerated. The composition fed to the reactor may have a relatively high catalyst to hydrocarbonaceous material mass ratio (e.g., from about 0.33:1 to about 20:1, or from about 0.5:1 to about 20:1, or from about 2:1 to about 10:1).

The expression that catalytic sites are positioned "in the pores near the pore mouth openings" refers to catalytic sites within the pores that are rendered inaccessible to the pyrolysis product as a result of treatment with the silicone compound. In an embodiment, these catalytic sites may be positioned within the pores at a depth of no more than about 10 angstroms from the pore mouth openings, or no more than about 7 angstroms, or no more than about 5 angstroms, or no more than about 2 angstroms, from the pore mouth openings. These catalytic sites may be inhibited or inoperative as a result of treatment with the silicone compound. That is, these catalysts may be deactivated as a result of the treatment with the silicone compound.

The inventive method may comprise a single-stage method for the pyrolysis of the hydrocarbonaceous material. This method may comprise providing or using a single-stage pyrolysis apparatus. A single-stage pyrolysis apparatus may be one in which pyrolysis and subsequent catalytic reactions are carried out in a single vessel. The single-stage pyrolysis apparatus may comprise a continuously stirred tank reactor, a bath reactor, a semi-batch reactor, a fixed bed reactor or a fluidized bed reactor. Multi-stage apparatuses may also be used for the production of fluid hydrocarbon products in accordance with the invention.

The hydrocarbonaceous material may comprise solids of any suitable size. In some cases, it may be advantageous to use hydrocarbonaceous solids with relatively small particle sizes. Small-particle solids may, in some instances, react more quickly than larger solids due to their relatively higher surface area to volume ratios compared to larger solids. In addition, small particle sizes may allow for more efficient heat transfer within each particle and/or within the reactor volume. This may prevent or reduce the formation of undesired reaction products. Moreover, small particle sizes may provide for increased solid-gas and solid-solid contact, leading to improved heat and mass transfer.

The average particle size of the solid hydrocarbonaceous material may be less than about 5 mm, less than about 2 mm, less than about 1 mm, less than about 500 microns, less than about 60 mesh (250 microns), less than about 100 mesh (149 microns), less than about 140 mesh (105 microns), less than about 170 mesh (88 microns), less than about 200 mesh (74 microns), less than about 270 mesh (53 microns), or less than about 400 mesh (37 microns), or smaller.

It may be desirable to employ a feed material with an average particle size above a minimum amount in order to reduce the pressure required to pass the solid hydrocarbonaceous feed material through the reactor. For example, it may be desirable to use a solid hydrocarbonaceous feed material with an average particle size of at least about 400 mesh (37 microns), at least about 270 mesh (53 microns), at least about 200 mesh (74 microns), at least about 170 mesh (88 microns), at least about 140 mesh (105 microns), at least about 100 mesh (149 microns), at least about 60 mesh (250 microns), at least about 500 microns, a least about 1 mm, at least about 2 mm, at least about 5 mm, or higher.

The hydrocarbonaceous material may comprise biomass. The hydrocarbonaceous material may comprise plastic waste, recycled plastics, agricultural and/or municipal solid waste, food waste, animal waste, carbohydrates, lignocellulosic materials (e.g., wood chips or shavings), or a mixture of two or more thereof. The hydrocarbonaceous material may comprise xylitol, glucose, cellobiose, cellulose, hemi-cellulose, lignin, or a mixture of two or more thereof. The hydrocarbonaceous material may comprise sugar cane bagasse, glucose, wood, corn stover, or a mixture of two or more thereof. The hydrocarbonaceous material may comprise wood.

Biomass pyrolysis liquid or bio-oil may be formed during the pyrolyzing step of the inventive method. Biomass pyrolysis liquid may be dark brown and may approximate to biomass in elemental composition. It may be composed of a very complex mixture of oxygenated hydrocarbons with an appreciable proportion of water from both the original moisture and reaction product. Compositionally, biomass pyrolysis oil may vary with the type of biomass, but is known to contain oxygenated low molecular weight alcohols (e.g., furfuryl alcohol), aldehydes (aromatic aldehydes), ketones (furanone), phenols (methoxy phenols) and water. Solid char may also be present, suspended in the oil. The liquid may be formed by rapidly quenching the intermediate products of flash pyrolysis of hemicellulose, cellulose and lignin in the

biomass. Chemically, the oil may contain several hundred different chemicals in widely varying proportions, ranging from formaldehyde and acetic acid to complex high molecular weight phenols, anhydrosugars and other oligosaccharides. It may have a distinctive odor from low molecular weight aldehydes and acids, and may be acidic with a pH of about 1.5 to about 3.8, and can be an irritant.

The residence time of the catalyst in the reactor may be defined as the volume of the reactor filled with catalyst divided by the volumetric flow rate of the catalyst through the reactor. For example if a 3 liter reactor contains 2 liters of catalyst and a flow of 0.4 liters per minute of catalyst is fed through the reactor, i.e., both fed and removed, the catalyst residence time will be 2/0.4 minutes, or 5 minutes.

The residence time of the catalyst in the reactor may be at least about 1 minute, at least about 2 minutes, at least about 5 minutes, at least about 7 minutes, at least about 10 minutes, at least about 15 minutes, at least about 20 minutes, at least about 25 minutes, at least about 30 minutes, at least about 60 minutes, or at least about 120 minutes. In some cases, the residence time of the catalyst in the reactor may be less than about 120 minutes, or from about 1 minute and about 120 minutes, or from about 2 minutes to about 120 minutes, or from about 5 minutes to about 120 minutes, or from about 7 minutes to about 120 minutes, or from about 10 minutes to about 120 minutes, or from about 12 minutes to about 120 minutes, or from about 15 minutes to about 120 minutes, or from about 20 minutes to about 120 minutes, or from about 30 minutes to about 120 minutes, or from about 60 minutes to about 120 minutes. In some cases, the use of relatively long residence times may allow for additional chemical reactions to form desirable products. Long catalyst residence times may be achieved by, for example, increasing the volume of the reactor and/or reducing the volumetric flow rate of the catalyst. The residence time of the catalyst may be relatively short, e.g., less than about 120 minutes, or less than about 60 minutes.

Contact time may be defined as the residence time of a material in a reactor or other device, when measured or calculated under standard conditions of temperature and pressure (i.e., 0°C and 100 kPa absolute pressure). For example, a 2 liter reactor to which is fed 3 standard liters per minute of gas has a contact time of 2/3 minute, or 40 seconds for that gas. For a chemical reaction, contact time or residence time is based on the volume of the reactor where substantial reaction is occurring; and would exclude

volume where substantially no reaction is occurring such as an inlet or an exhaust conduit. For catalyzed reactions, the volume of a reaction chamber is the volume where catalyst is present.

The term "conversion of a reactant" may refer to the reactant mole or mass change between a material flowing into a reactor and a material flowing out of the reactor divided by the moles or mass of reactant in the material flowing into the reactor. For example, if 100 g of ethylene are fed to a reactor and 30 g of ethylene are flowing out of the reactor, the conversion is [(100 – 30) / 100] = 70% conversion of ethylene.

The term "fluid" may refer to a gas, a liquid, a mixture of a gas and a liquid, or a gas or a liquid containing dispersed solids, liquid droplets and/or gaseous bubbles. The terms "gas" and "vapor" have the same meaning and are sometimes used interchangeably. In some embodiments, it may be advantageous to control the residence time of the fluidization fluid in the reactor. The fluidization residence time of the fluidization fluid is defined as the volume of the reactor divided by the volumetric flow rate of the fluidization fluid under process conditions of temperature and pressure.

The term "fluidized bed reactor" may be used to refer to reactors comprising a vessel that contains a granular solid material (e.g., silica particles, catalyst particles, etc.), in which a fluid (e.g., a gas or a liquid) is passed through the granular solid material at velocities sufficiently high as to suspend the solid material and cause it to behave as though it were a fluid. The term "circulating fluidized bed reactor" may be used to refer to fluidized bed reactors in which the granular solid material is passed out of the reactor, circulated through a line in fluid communication with the reactor, and recycled back into the reactor.

Bubbling fluidized bed reactors and turbulent fluidized bed reactors may be used. In bubbling fluidized bed reactors, the fluid stream used to fluidize the granular solid material may be operated at a sufficiently low flow rate such that bubbles and voids may be observed within the volume of the fluidized bed during operation. In turbulent fluidized bed reactors, the flow rate of the fluidizing stream will be higher than that employed in a bubbling fluidized bed reactor. Examples of fluidized bed reactors, circulating fluidized bed reactors, bubbling and turbulent fluidized bed reactors are described in Kirk-Othmer Encyclopedia of Chemical Technology (online), Vol. 11,

Hoboken, N.J.: Wiley Interscience, 2001, pages 791-825, these pages being incorporated herein by reference.

The terms “olefin” or “olefin compound” (a.k.a. “alkenes”) may be used to refer to any unsaturated hydrocarbon containing one or more pairs of carbon atoms linked by a double bond. Olefins may include both cyclic and acyclic (aliphatic) olefins, in which the double bond is located between carbon atoms forming part of a cyclic (closed-ring) or of an open-chain grouping, respectively. In addition, olefins may include any suitable number of double bonds (e.g., monoolefins, diolefins, triolefins, etc.). Examples of olefin compounds may include ethene, propene, allene (propadiene), 1-butene, 2-butene, isobutene (2 methyl propene), butadiene, and isoprene, among others. Examples of cyclic olefins may include cyclopentene, cyclohexane, cycloheptene, among others. Aromatic compounds such as toluene are not considered olefins; however, olefins that include aromatic moieties are considered olefins, for example, benzyl acrylate or styrene.

Pore size relates to the size of a molecule or atom that can penetrate into the pores of a material. As used herein, the term "pore size" for zeolites refers to the Norman radii adjusted pore size. Determination of Norman radii adjusted pore size is described, for example, in Cook, M.; Conner, W. C., "How big are the pores of zeolites?" Proceedings of the International Zeolite Conference, 12th, Baltimore, July 5-10, 1998; (1999), 1, pp 409-414, which is incorporated herein by reference. As a specific exemplary calculation, the atomic radii for ZSM-5 pores are about 5.5-5.6 Angstroms, as measured by x-ray diffraction. In order to adjust for the repulsive effects between the oxygen atoms in the catalyst, Cook and Conner have shown that the Norman adjusted radii are 0.7 Angstroms larger than the atomic radii (about 6.2-6.3 Angstroms).

One of ordinary skill in the art will understand how to determine the pore size (e.g., minimum pore size, average of minimum pore sizes) in a catalyst. For example, x-ray diffraction (XRD) may be used to determine atomic coordinates. XRD techniques for the determination of pore size are described, for example, in Pecharsky, V.K. et at, "Fundamentals of Powder Diffraction and Structural Characterization of Materials," Springer Science+Business Media, Inc., New York, 2005, incorporated herein by reference in its entirety. Other techniques that may be useful in determining pore sizes (e.g., zeolite pore sizes) may include, for example, helium pycnometry or low pressure argon adsorption techniques. These and other techniques are described in Magee, J.S. et

at, "Fluid Catalytic Cracking: Science and Technology," Elsevier Publishing Company, July 1, 1993, pp. 185-195, which is incorporated herein by reference in its entirety. Pore sizes of mesoporous catalysts may be determined using, for example, nitrogen adsorption techniques, as described in Gregg, S. J. at al, "Adsorption, Surface Area and Porosity," 2nd Ed., Academic Press Inc., New York, 1982 and Rouquerol, F. et al, "Adsorption by powders and porous materials. Principles, Methodology and Applications," Academic Press Inc., New York, 1998, both of which are incorporated herein by reference.

A screening method may be used to select catalysts with appropriate pore sizes for the conversion of specific pyrolysis product molecules. The screening method may comprise determining the size of pyrolysis product molecules desired to be catalytically reacted (e.g., the molecule kinetic diameters of the pyrolysis product molecules). One of ordinary skill in the art may calculate, for example, the kinetic diameter of a given molecule. The type of catalyst may then be chosen such that the pores of the catalyst (e.g., Norman adjusted minimum radii) are sufficiently large to allow the pyrolysis product molecules to diffuse into and/or react with the catalyst. In some embodiments, the catalysts may be chosen such that their pore sizes are sufficiently small to prevent entry and/or reaction of pyrolysis products whose reaction would be undesirable.

The catalyst may comprise any catalyst suitable for conducting the catalytically reacting step of the inventive method. The catalyst may be used to lower the activation energy (increase the rate) of the reaction conducted in the catalytically reacting step and/or improve the distribution of products or intermediates during the reaction (for example, a shape selective catalyst). Examples of reactions that can be catalyzed include: dehydration, dehydrogenation, isomerization, hydrogen transfer, aromatization, decarbonylation, decarboxylation, aldol condensation, and combinations thereof. The catalyst components may be acidic, neutral or basic.

The inventive method may comprise a CFP process. For CFP processes, particularly advantageous catalysts may include those containing internal porosity selected according to pore size (e.g., mesoporous and pore sizes typically associated with zeolites), e.g., average pore sizes of less than about 100 Angstroms, less than about 50 Angstroms, less than about 20 Angstroms, less than about 10 Angstroms, less than about 5 Angstroms, or smaller. In some embodiments, catalysts with average pore sizes of from about 5 Angstroms to about 100 Angstroms may be used. In some embodiments,

catalysts with average pore sizes of between about 5.5 Angstroms and about 6.5 Angstroms, or between about 5.9 Angstroms and about 6.3 Angstroms may be used. In some cases, catalysts with average pore sizes of between about 7 Angstroms and about 8 Angstroms, or between about 7.2 Angstroms and about 7.8 Angstroms may be used.

The catalyst may be selected from naturally occurring zeolites, synthetic zeolites and combinations thereof. The catalyst may comprise a ZSM-5 zeolite catalyst. The catalyst may comprise acid sites. These acid sites may also be referred to as catalytically active sites. Other zeolite catalysts that may be used may include ferrierite, zeolite Y, zeolite beta, mordenite, MCM-22, ZSM-23, ZSM-57, SUZ-4, EU-1, ZSM-11, (S)A1P0-31, SSZ-23, and the like. The catalyst may comprise silica and alumina, and further comprise one or more additional metals and/or a metal oxides. Suitable metals and/or oxides may include, for example, nickel, palladium, platinum, titanium, vanadium, chromium, manganese, iron, cobalt, zinc, copper, gallium, and/or any of their oxides, among others. In some cases promoter elements selected from the rare earth elements, i.e., elements 57-71, cerium, zirconium or their oxides, or combinations of these may be included to modify the activity, structure and/or stability of the catalyst. In addition, in some cases, properties of the catalysts (e.g., pore structure, type and/or number of catalytic sites, etc.) may be chosen to selectively produce a desired product.

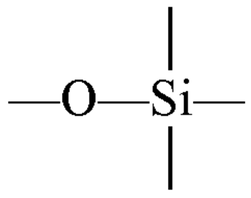
The catalyst may be treated or impregnated one or more times with a silicone compound to reduce the size of the pore mouth openings in the catalyst as well as cover or obscure catalytic sites on the external surface of the catalyst and inside the pores of the catalyst near the pore mouth openings. The covering of the catalytic sites with the treatment layer may inhibit and/or extinguish their catalytic activity. In order to facilitate a more controlled application of the silicone compound, the silicone compound may be dispersed in a carrier, for example, an aqueous or organic liquid carrier.

In each phase of the catalyst treatment process, the silicone compound may be deposited on the external surface of the catalyst by any suitable method. For example, the silicone compound may be dissolved in an organic carrier, mixed with the catalyst, and then dried by evaporation or vacuum distillation. The catalyst may be contacted with the silicone compound at a catalyst to silicone compound weight ratio in the range from about 1000:1 to about 1:10.

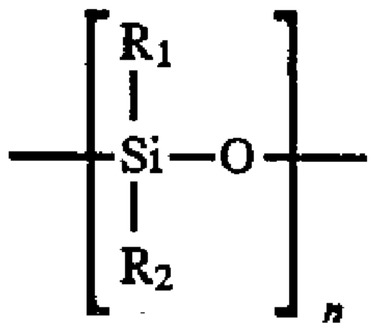
The silicone compound may be provided in the form of a solution or an emulsion under the conditions of contact with the catalyst. The deposited silicone compound may cover, and reside substantially exclusively on, the external surface of the catalyst, blocking external sites and partially blocking pore mouths and sites in or near the pore mouths openings. Examples of methods of depositing silicone compounds on the surface of zeolites may be found in U.S. Patents 4,090,981; 5,243,117; 5,403,800, and 5,659,098, which are incorporated by reference herein.

The catalyst may be ex situ treated by single or multiple coatings with the silicone compound, each coating followed by calcination. The coated catalyst may comprise silica and alumina. The silica to alumina molar ratio may be in the range from about 10:1 to about 50:1, or in the range from about 10:1 to about 40:1, or in the range from about 10:1 to about 20:1, or about 15:1. The coated catalyst may further comprise nickel, platinum, vanadium, palladium, manganese, cobalt, zinc, copper, chromium, gallium, an oxide of one or more thereof, or a mixture of two or more thereof.

The term "silicone compound" is used herein to refer to any compound that contains one or more Si-O groups. The silicone compound may be a silicate containing one or more of SiO_4^{4-}, $Si_2O_7^{6-}$ or $Si_6O_{18}^{12-}$ groups. These may include one or more tetraorthosilicates. The silicone compound may include one or more siloxanes containing one or more silicon-oxygen backbones (-Si-O-Si-O-) with organic (e.g., hydrocarbon) side groups attached to the silicon atoms. These may include one or more siloxane polymers (e.g., polydimethyl siloxane). The silicone compound may be a straight chain, branched chain or cyclical compound. The silicone compound may be monomeric, oligomeric or polymeric. The silicone compound may comprise a compound containing at least one group represented by the formula



The silicone compound may be represented by the formula:



wherein R_1 and R_2 independently comprise hydrogen, halogen, hydroxyl, alkyl, alkoxyl, halogenated alkyl, aryl, halogenated aryl, aralkyl, halogenated aralkyl, alkaryl or halogenated alkaryl; and n is a number that is at least 2. R_1 and/or R_2 may comprise methyl, ethyl or phenyl. n may be a number in the range from about 3 to about 1000.

The silicone compound may have a number average molecular weight in the range from about 80 to about 20,000, or from about 150 to 10,000.

The silicone compound may comprise dimethylsilicone, diethylsilicone, phenylmethylsilicone, methylhydrogensilicone, ethylhydrogen silicone, phenylhydrogen silicone, methylethyl silicone, phenylethyl silicone, diphenyl silicone, methyltrifluoropropyl silicone, ethyltrifluoropropyl silicone, polydimethyl silicone, tetrachloro-phenylmethyl silicone, tetrachlorophenylethyl silicone, tetrachlorophenylhydrogen silicone, tetrachlorophenylphenyl silicone, methylvinyl silicone, hexamethyl cyclotrisiloxane, octamethyl cyclotetrasiloxane, hexaphenyl cyclotrisiloxane, octaphenyl cyclotetrasiloxane, or a mixture of two or more thereof.

The silicone compound may comprise a tetraorthosilicate. The silicone compound may comprise tetramethylorthosilicate, tetraethylorthosilicate, or a mixture thereof.

The kinetic diameter of the silicone compound may be larger than the pore diameter of the catalyst in order to avoid entry of the silicone compound into the pore and any concomitant reduction in the internal activity of the catalyst.

The organic carrier for the silicone compound may comprise hydrocarbons such as linear, branched, and cyclic alkanes having five or more carbons. The carrier may comprise a linear, branched or cyclic alkane having a boiling point greater than about 70°C, and containing about 6 or more carbons. Optionally, mixtures of low volatility organic compounds, such as hydrocracker recycle oil, may also be employed as carriers. Low volatility hydrocarbon carriers for the silicone compound may comprise decane, dodecane, mixtures thereof, and the like.

Following each deposition of the silicone compound, the catalyst may be calcined to decompose the molecular or polymeric species to a solid state species. The catalyst may be calcined at a rate of from about 0.2° C/minute to about 5° C/minute to a temperature greater than about 200°C, but below a temperature at which the crystallinity of the zeolite may be adversely affected. Generally, such temperature will be below about 600°C. The temperature of calcination may be in the range from about 350°C to about 550°C. The catalyst may be maintained at the calcination temperature for about 1 to about 24 hours, or about 2 to about 6 hours.

The catalyst may be treated with a tetraorthosilicate using a chemical liquid deposition (CLD) process. The tetraorthosilicate may comprise tetramethylorthosilicate, tetraethylorthosilicate (TEOS), or a mixture thereof. The CLD process may comprise dispersing the catalyst in a liquid medium (e.g., hexanes, alkanes, aromatics or other non-polar organic solvent) at a concentration in the range from about 0.1 to about 20% by weight, or from about 1 to about 10% by weight; adding the tetraorthosilicate to provide a mixture containing from about 0.01 to about 5% by weight, or from about 0.1 to about 1% by weight of the tetraorthosilicate; refluxing the resulting mixture at an elevated temperature (e.g., in the range from about 50 to about 150°C, or about 90°C) with stirring; recovering the catalyst (e.g., via centrifuging) from the liquid medium; drying the catalyst; and then calcining the catalyst in air at a temperature in the range from about 100 to about 550°C, or from about 150 to about 325°C, for a time period in the range from about 1 to about 24 hours, or about 2 to about 12 hours . This procedure may be repeated any desired number of times (e.g., 1, 2, 3 additional times, etc.), to provide for the desired treatment layer derived from the tetraorthosilicate. When using TEOS as the tetraorthosilicate, this process may be referred to as a TEOS CLD silylation process.

While not wishing to be bound by theory, it is believed that the advantages of treatment with silicone compounds are in part obtained by rendering active catalytic sites on the external surfaces of the catalyst substantially inaccessible to reactants, while increasing catalyst tortuosity by reducing the size of the pore mouth openings. Active catalytic sites existing on the external surface of the catalyst are believed to isomerize the para-isomer back to an equilibrium level with the other two isomers. Thus, by reducing the availability of these active catalytic sites, the relatively high proportion of para-

xylene may be maintained. It is believed that the silicone compounds of the present invention may block or otherwise render these external catalytic sites unavailable to the para-isomers by chemically modifying, covering, or obscuring the sites.

It may be beneficial to control the residence time of the reactants (e.g., the solid hydrocarbonaceous material and/or a non-solid reactant) and catalyst(s) in the reactor and/or under a defined set of reaction conditions (i.e. conditions under which the reactants may undergo pyrolysis or catalysis in a given reactor system).

The term "overall residence time" refers to the volume of a reactor or device or specific portion of a reactor or device divided by the exit flow of all gases out of the reactor or device including fluidization gas, products, and impurities, measured or calculated at the average temperature of the reactor or device and the exit pressure of the reactor or device.

The term "reactant residence time" of a reactant in the reactor is defined as the amount of time the reactant spends in the reactor. Residence time may be based on the feed rate of reactant and is independent of rate of reaction. The reactant residence time of the reactants in a reactor may be calculated using different methods depending upon the type of reactor being used. For gaseous reactants, where flow rate into the reactor is known, this is typically a simple calculation. In the case of solid reactants in which the reactor comprises a packed bed reactor into which only reactants are continuously fed (i.e. no carrier or fluidizing flow is utilized), the reactant residence time in the reactor may be calculated by dividing the volume of the reactor by the volumetric flow rate of the hydrocarbonaceous material and fluid hydrocarbon product exiting the reactor.

In cases where the reaction takes place in a reactor that is closed to the flow of mass during operation (e.g., a batch reactor), the batch residence time of the reactants in such may be reactor is defined as the amount of time elapsing between the time at which the temperature in the reactor containing the reactants reaches a level sufficient to commence a pyrolysis reaction (e.g., for CFP, typically about 300 °C to about 1000 °C for many typical hydrocarbonaceous feedstock materials) and the time at which the reactor is quenched (e.g., cooled to a temperature below that sufficient to support further pyrolysis - e.g. typically about 300 °C to about 1000 °C for many hydrocarbonaceous feedstock materials).

In some cases, e.g. for certain fluidized bed reactors, the reactor feed stream(s) may include feed stream(s) comprising auxiliary materials (i.e., matter other than solid hydrocarbonaceous materials and/or non-solid reactants). For example, in certain cases where fluidized beds are used as reactors, the feed stream may comprise fluidization fluid(s). In cases where circulating fluidized beds are used, catalyst and fluidization fluid may both be fed, recycled, or fed and recycled to the reactor. In such cases, the reactant residence time of the reactants in the reactor can be determined as the volume of the reactor divided by the volumetric flow rate of the reactants and reaction product gases exiting the reactor as with the packed bed situation described above; however, since the flow rate of the reactants and reaction product gases exiting the reactor may not be convenient to determine directly, the volumetric flow rate of the reactants and reaction product gases exiting the reactor may be estimated by subtracting the feed volumetric flow rate of the auxiliary materials (e.g., fluidization fluid, catalyst, contaminants, etc.) into the reactor from the total volumetric flow rate of the gas stream(s) exiting the reactor.

The term "selectivity" refers to the amount of production of a particular product in comparison to a selection of products. Selectivity to a product may be calculated by dividing the amount of a particular product by the amount of a number of products produced. For example, if 75 grams of aromatics are produced in a reaction and 20 grams of benzene are found in these aromatics, on a mass basis the selectivity to benzene amongst aromatic products is 20/75 = 26.7%. Selectivity may be calculated on a mass basis, as in the aforementioned example, or it may be calculated on a carbon basis where the selectivity is calculated by dividing the amount of carbon that is found in a particular product by the amount of carbon that is found in a selection of products. Unless specified otherwise, for reactions involving biomass as a reactant, selectivity is on a mass basis. For reactions involving conversion of a specific molecular reactant (ethene for example), selectivity is the percentage (on a mass basis unless specified otherwise) of a selected product divided by all the products produced. The selectivity for various materials can be determined using the following equations:

(1) Overall selectivity = $\frac{\textit{moles of carbon in a product}}{\textit{moles of carbon in all products}}$ x 100%

(2) Aromatic selectivity $= \frac{moles\ of\ carbon\ in\ an\ aromatic\ product}{moles\ of\ carbon\ in\ all\ aromatic\ products} \times 100\%$

(3) Olefin selectivity $= \frac{moles\ of\ carbon\ in\ an\ olefinic\ product}{moles\ of\ carbon\ in\ all\ olefins\ products} \times 100\%$

(4) p-Xylene selectivity in xylenes $= \frac{moles\ of\ p-xylene\ isomer}{moles\ of\ all\ xylene\ isomers} \times 100\%$

The term "yield" is used herein to refer to the amount of a product flowing out of a reactor divided by the amount of reactant flowing into the reactor, usually expressed as a percentage or fraction. Yields are often calculated on a mass basis, carbon basis, or on the basis of a particular feed component. Mass yield is the mass of a particular product divided by the weight of feed used to prepare that product. For example, if 500 grams of biomass is fed to a reactor and 45 grams of p-xylene is produced, the mass yield of p-xylene would be 45/500 = 9% p-xylene . Carbon yield is the mass of carbon found in a particular product divided by the mass of carbon in the feed to the reactor. For example, if 500 grams of biomass that contains 40% carbon is reacted to produce 45 g of p-xylene that contains 90.6% carbon, the carbon yield is [(45 * 0.906)/(500 * 0.40)] = 20.4%. Carbon yield from biomass is the mass of carbon found in a particular product divided by the mass of carbon fed to the reactor in a particular feed component. For example, if 500 grams of biomass containing 40% carbon and 100 grams of CO_2 are reacted to produce 40 g of p-xylene (containing 90.6% carbon), the carbon yield on biomass is [(40 * 0.906)/(500 * 0.40)] = 18.1%; note that the mass of CO_2 does not enter into the calculation.

The embodiments described herein may also involve chemical process designs used to perform catalytic pyrolysis. The processes may involve the use of one or more fluidized bed reactors (e.g., a circulating fluidized bed reactor, turbulent fluidized bed reactor, bubbling fluidized bed reactor, etc.). The process designs described herein may optionally involve specialized handling of the material fed to one or more reactors. For example, the feed material may be dried, cooled, and/or ground prior to supplying the material to a reactor. Other aspects of the invention may relate to product compositions produced using the process designs described herein.

Without being bound to a particular mode of action or order of steps of the overall thermal/catalytic conversion process, catalytic pyrolysis is believed to involve at

least partial thermal pyrolysis of hydrocarbonaceous material (e.g., solid biomass such as cellulose) to produce one or more pyrolysis products (e.g., volatile organics, gases, solid coke, etc.) and catalytic reaction of at least a portion of the one or more pyrolysis products using a catalyst under reaction conditions sufficient to produce fluid hydrocarbon products. The catalytic reaction may involve volatile organics entering into a catalyst (e.g., a zeolite catalyst) where they are converted into, for example, p-xylene as well as other hydrocarbons such as aromatics and olefins, in addition to carbon monoxide, carbon dioxide, water, and coke. Inside or upon contact with the catalyst, the pyrolysis product may undergo a series of dehydration, decarbonylation, decarboxylation, isomerization, oligomerization, and dehydrogenation reactions that lead to aromatics, olefins, CO, CO_2 and water. The catalysts provided for herein may be particularly suited for producing xylenes with a relatively high selectivity to p-xylene in the xylenes of at least about 40%, or at least about 45%, or at least about 50%, or at least about 55%, or at least about 60%, or at least about 65%, or at least about 70%, or at least about 75%, or at least about 80%, or at least about 85%, or at least about 90%.

FIG. 1A includes a schematic illustration of an exemplary chemical process design used to perform catalytic pyrolysis, according to the inventive method. The process may comprise a CFP process. Referring to FIG. 1A, feed stream 10 includes a solid hydrocarbonaceous material that can be fed to reactor 20. The solid hydrocarbonaceous material may generally comprise at least carbon and hydrogen. In certain solid hydrocarbonaceous materials (e.g. wood), carbon may be the most abundant component by mass, while in others (e.g. glucose) oxygen may be more abundant than carbon. Certain solid hydrocarbonaceous materials may also comprise relatively minor proportions of other elements such as nitrogen and sulfur.

The feed streams to the reactor may be free of olefins, or may contain olefins in an insignificant amount (e.g., such that olefins make up less than about 1 wt%, less than about 0.1 wt%, or less than about 0.01 wt% of the total weight of reactant fed to the reactor). In other embodiments, however, olefins may be present in one or more reactant feed streams.

The solid hydrocarbonaceous material feed composition (e.g., in feed stream 10 of FIG. 1A) may comprise a mixture of solid hydrocarbonaceous material and a catalyst. The mixture may comprise, for example, a solid catalyst and a solid hydrocarbonaceous material. In other embodiments, a catalyst may be provided separately from the solid

hydrocarbonaceous material (e.g., by co-feeding the catalyst via an independent catalyst inlet). A variety of catalysts may be used. For example, in some instances, zeolite catalysts with varying molar ratios of silica to alumina, and/or varying pore sizes and/or pore opening sizes, and/or varying catalytically active metals and/or metal oxides, may be used.

Moisture 12 may optionally be removed from the solid hydrocarbonaceous feed composition prior to being fed to the reactor, e.g., by an optional dryer 14. Removal of moisture from the solid hydrocarbonaceous material feed stream may be advantageous for several reasons. For example, the moisture in the feed stream may require additional energy input in order to heat the solid hydrocarbonaceous material to a temperature sufficiently high to achieve pyrolysis. Variations in the moisture content of the solid hydrocarbonaceous feed may lead to difficulties in controlling the temperature of the reactor. In addition, removal of moisture from the solid hydrocarbonaceous feed can reduce or eliminate the need to process the water during later processing steps.

The solid hydrocarbonaceous feed composition may be dried until the solid hydrocarbonaceous feed composition comprises less than about 10%, less than about 5%, less than about 2%, or less than about 1% water by weight. Suitable equipment capable of removing water from the feed composition is known to those skilled in the art. As an example, the dryer may comprise an oven heated to a particular temperature (e.g., at least about 80 °C, at least about 100 °C, at least about 150 °C, or higher) through which the solid hydrocarbonaceous feed composition may continuously, semi-continuously, or periodically pass. The dryer may comprise a vacuum chamber into which the solid hydrocarbonaceous feed composition may be processed as a batch. The dryer may combine elevated temperatures with vacuum operation. The dryer may be integrally connected to the reactor or may be provided as a separate unit from the reactor.

The particle size of the solid hydrocarbonaceous feed composition may be reduced in an optional grinding system 16 prior to passing the solid hydrocarbonaceous feed to the reactor. The average diameter of the ground, solid hydrocarbonaceous feed composition exiting the grinding system may comprise no more than about 50%, no more than about 25%, no more than about 10%, no more than about 5%, no more than about 2% of the average diameter of the feed composition fed to the grinding system. Large-particle solid hydrocarbonaceous feed material may be more easily transportable and less messy than

small-particle feed material. On the other hand, in some cases it may be advantageous to feed small particles of solid hydrocarbonaceous material to the reactor. The use of a grinding system allows for the transport of large-particle solid hydrocarbonaceous feed between the source and the process, while enabling the feed of small particles to the reactor.

Suitable equipment capable of grinding the solid hydrocarbonaceous feed composition is known to those skilled in the art. For example, the grinding system may comprise an industrial mill (e.g., hammer mill, ball mill, etc.), a unit with blades (e.g., chipper, shredder, etc.), or any other suitable type of grinding system. The grinding system may comprise a cooling system (e.g., an active cooling systems such as a pumped fluid heat exchanger, a passive cooling system such as one including fins, etc.), which may be used to maintain the solid hydrocarbonaceous feed composition at relatively low temperatures (e.g., ambient temperature) prior to introducing the solid hydrocarbonaceous feed composition to the reactor. The grinding system may be integrally connected to the reactor or may be provided as a separate unit from the reactor. While the grinding step is shown following the drying step in FIG. 1A, the order of these operations may be reversed in some embodiments. In still other embodiments, the drying and grinding steps may be achieved using an integrated unit.

Grinding and cooling of the solid hydrocarbonaceous material may be achieved using separate units. Cooling of the solid hydrocarbonaceous material may be desirable, for example, to reduce or prevent unwanted decomposition of the solid hydrocarbonaceous feed material prior to passing it to the reactor. The solid hydrocarbonaceous material may be passed to a grinding system to produce a ground solid hydrocarbonaceous material. The ground solid hydrocarbonaceous material may then be passed from the grinding system to a cooling system and cooled. The solid hydrocarbonaceous material may be cooled to a temperature lower than about 300 °C, lower than about 200 °C, lower than about 100 °C, lower than about 75 °C, lower than about 50 °C, lower than about 35 °C, or lower than about 20 °C prior to introducing the solid hydrocarbonaceous material into the reactor. The cooling system may include an active cooling unit (e.g., a heat exchanger) capable of lowering the temperature of the solid hydrocarbonaceous material. The two or more of the drier, grinding system, and cooling system may be combined in a single unit. The cooling system may be directly integrated with one or more reactors.

The hydrocarbonaceous material may be transferred to reactor 20. The reactor may be used, in some instances, to perform catalytic pyrolysis of at least a portion of the first reactant comprising the hydrocarbonaceous material under reaction conditions sufficient to produce one or more pyrolysis products. In the illustrative embodiment of FIG. 1A, the reactor comprises any suitable reactor known to those skilled in the art. For example, in some instances, the reactor may comprise a continuously stirred tank reactor (CSTR), a batch reactor, a semi-batch reactor, or a fixed bed catalytic reactor, among others. In some cases, the reactor comprises a fluidized bed reactor, e.g., a circulating fluidized bed reactor. Fluidized bed reactors may, in some cases, provide improved mixing of the catalyst, solid hydrocarbonaceous material during pyrolysis and/or subsequent reactions, which may lead to enhanced control over the reaction products formed. The use of fluidized bed reactors may also lead to improved heat transfer within the reactor. In addition, improved mixing in a fluidized bed reactor may lead to a reduction of the amount of coke adhered to the catalyst, resulting in reduced deactivation of the catalyst in some cases.

The reactor(s) may have any suitable size for performing the processes described herein. For example, the reactor may have a volume between about 0.1-1 L, 1-50 L, 50-100 L, 100-250 L, 250-500 L, 500-1000 L, 1000-5000 L, 5000-10,000 L, or 10,000-50,000 L. In some instances, the reactor may have a volume greater than about 1 L, or in other instances, greater than about 10 L, 50 L, 100 L, 250 L, 500 L, 1,000 L, or 10,000 L. Reactor volumes greater than about 50,000 L may also be possible. The reactor may be cylindrical, spherical, or any other suitable shape.

Higher yields of desired product formation, lower yields of coke formation, and/or more controlled product formation (e.g., higher production of p-xylene relative to other products) may be achieved when particular combinations of reaction conditions and system components are implemented in methods and systems described herein. For example, conditions such as the mass normalized space velocity(ies) (e.g., of the solid hydrocarbonaceous material and/or the fluidization fluid), the temperature of the reactor and/or solids separator, the reactor pressure, the heating rate of the feed stream(s), the catalyst to solid hydrocarbonaceous material mass ratio, the residence time of the hydrocarbonaceous material in the reactor, the residence time of the reaction products in the solids separator, and/or the catalyst type (as well as silica to alumina molar ratio and

pore mouth opening size) may be controlled to achieve beneficial results, as described below.

The reactor(s) may be operated at any suitable temperature. In some instances, it may be desirable to operate the reactor(s) at intermediate temperatures, compared to temperatures typically used in many previous catalytic pyrolysis systems. For example, the reactor may be operated at temperatures of between about 400 °C and about 600 °C, between about 425 °C and about 500 °C, or between about 440 °C and about 460 °C. Operating the reactor(s) at these intermediate temperatures may allow one to maximize the amount of desirable products. The invention may not be limited to the use of such intermediate temperatures, however, and in other embodiments, lower and/or higher temperatures can be used.

The reactor(s) may also be operated at any suitable pressure. The reactor may be operated at a pressure of at least about 100 kPa, or at least about 200 kPa, or at least about 300 kPa, or at least about 400 kPa. The reactor may be operated at a pressure below about 600 kPa, or below about 400 kPa, or below about 200 kPa. The reactor may be operated at a pressure in the range from about 100 to about 600 kPa, or in the range from about 100 to about 400 kPa, or in the range from about 100 to about 200 kPa. The invention may not be limited to the use of such pressures, however, and in other embodiments, lower and/or higher pressures may be employed.

It may be advantageous to heat the feed stream(s) at a relatively fast rate as it enters the reactor. High heating rates may be advantageous for a number of reasons. For instance, high heating rates may enhance the rate of mass transfer of the reactants from the bulk solid hydrocarbonaceous material to the catalytic reactant sites. This may, for example, facilitate introduction of volatile organic compounds formed during the pyrolysis of the solid hydrocarbonaceous material into the catalyst before completely thermally decomposing the solid hydrocarbonaceous material and/or the second reactant into generally undesired products (e.g., coke). In addition, high heating rates may reduce the amount of time the reactants are exposed to low temperatures (i.e., temperatures between the temperature of the feed and the desired reaction temperature). Prolonged exposure of the reactants to low temperatures may lead to the formation of undesirable products via undesirable decomposition and/or reaction pathways. Examples of suitable heating rates for heating the feed stream(s) upon entering the reactor may include, for

example, greater than about 50°C/s, greater than about 100 °C/s, greater than about 200 °C/s, greater than about 300 °C/s, greater than about 400 °C/s, greater than about 500 °C/s, greater than about 600 °C/s, greater than about 700 °C/s, greater than about 800 °C/s, greater than about 900 °C/s, greater than about 1000 °C/s, or greater. In some cases, the reactant(s) may be heated at a heating rate of between about 500 °C/s and about 1000 °C/s. In some embodiments, the heating rate for heating the feed stream(s) upon entering the reactor may be between about 50 °C/s and about 1000 °C/s, or between about 50 °C/s and about 400 °C/s. The invention may not limited to the use of such heating rates, however, and in other embodiments, lower and/or higher heating rates can be used.

The mass-normalized space velocity of the hydrocarbonaceous material may be selected to selectively produce a desired array of fluid hydrocarbon products. As used herein, the term "mass-normalized space velocity" of a component is defined as the mass flow rate of the component into the reactor (e.g., as measured in g/hr) divided by the mass of catalyst in the reactor (e.g., as measured in g) and has units of inverse time. For example, the mass-normalized space velocity of solid hydrocarbonaceous material fed to the reactor may be calculated as the mass flow rate of the solid hydrocarbonaceous material into the reactor divided by the mass of catalyst in the reactor. The mass-normalized space velocity of a component (e.g., the hydrocarbonaceous material) in the reactor may be calculated using different methods depending upon the type of reactor being used. For example, in systems employing batch or semi-batch reactors, wherein the solid hydrocarbonaceous material is not fed continuously to the reactor, the solid hydrocarbonaceous material does not have a mass-normalized space velocity. For systems in which catalyst is fed to and/or extracted from the reactor during reaction (e.g., circulating fluidized bed reactors), the mass-normalized space velocity may be determined by calculating the average amount of catalyst within the volume of the reactor over a period of operation (e.g., steady-state operation).

The mass-normalized space velocity of the hydrocarbonaceous material fed to the reactor may be at a mass normalized space velocity of up to about 3 $hour^{-1}$, or up to about 2 $hour^{-1}$, or up to about 1.5 $hour^{-1}$, or up to about 0.9 $hour^{-1}$, or in the range from about 0.01 $hour^{-1}$ to about 3 $hour^{-1}$, or in the range from about 0.01 to about 2 $hour^{-1}$, or in the range from about 0.01 to about 1.5 $hour^{-1}$, or in the range from about 0.01 to about

0.9 hour^{-1}, or in the range from about 0.01 hour^{-1} to about 0.5 hour^{-1}, or in the range from about 0.1 hour^{-1} to about 0.9 hour^{-1}, or in the range from about 0.1 hour^{-1} to about 0.5 hour^{-1}. The invention may not be limited to the use of such mass-normalized space velocities, however, and in other embodiments, lower and/or higher mass-normalized space velocities can be used.

The residence time of a reactant (e.g., the hydrocarbonaceous material) in the reactor (i.e., the reactant residence time) may be at least about 1 second, at least about 2 seconds, at least about 5 seconds, at least about 7 seconds, at least about 10 seconds, at least about 15 seconds, at least about 20 seconds, at least about 25 seconds, at least about 30 seconds, at least about 60 seconds, at least about 120 seconds, at least about 240 seconds, or at least about 480 seconds. In some cases, the residence time of a reactant (e.g., the hydrocarbonaceous material) in the reactor may be less than about 5 minutes, or from about 1 second and about 4 minutes, or from about 2 seconds to about 4 minutes, or from about 5 seconds to about 4 minutes, or from about 7 seconds to about 4 minutes, or from about 10 seconds to about 4 minutes, or from about 12 seconds to about 4 minutes, or from about 15 seconds to about 4 minutes, or from about 20 seconds to about 4 minutes, or from about 30 seconds to about 4 minutes, or from about 60 seconds to about 4 minutes. Previous "fast pyrolysis" studies have, in many cases, employed systems with very short reactant residence times (e.g., less than 2 seconds). In some cases, however, the use of relatively longer residence times may allow for additional chemical reactions to form desirable products. Long residence times may be achieved by, for example, increasing the volume of the reactor and/or reducing the volumetric flow rate of the hydrocarbonaceous materials. It should be understood, however, that in some embodiments described herein, the residence time of the reactant (e.g., hydrocarbonaceous material) may be relatively shorter, e.g., less than about 2 seconds, or less than about 1 second.

The contact time of the pyrolysis product (e.g., pyrolysis vapor) with the catalyst in the reactor may be at least about 1 second, at least about 2 seconds, at least about 5 seconds, at least about 7 seconds, at least about 10 seconds, at least about 15 seconds, at least about 20 seconds, at least about 25 seconds, at least about 30 seconds, at least about 60 seconds, at least about 120 seconds, at least about 240 seconds, or at least about 480 seconds. The contact time may be less than about 5 minutes, or from about 1 second

and about 4 minutes, or from about 2 seconds to about 4 minutes, or from about 5 seconds to about 4 minutes, or from about 7 seconds to about 4 minutes, or from about 10 seconds to about 4 minutes, or from about 12 seconds to about 4 minutes, or from about 15 seconds to about 4 minutes, or from about 20 seconds to about 4 minutes, or from about 30 seconds to about 4 minutes, or from about 60 seconds to about 4 minutes.

In certain cases where fluidized bed reactors are used, the feed material (e.g., a solid hydrocarbonaceous material) in the reactor may be fluidized by flowing a fluid stream through the reactor. In the exemplary embodiment of FIG. 1A, a fluid stream 44 is used to fluidize the feed material in reactor 20. Fluid may be supplied to the fluid stream from a fluid source 24 and/or from the product streams of the reactor via a compressor 26. As used herein, the term "fluid" means a material generally in a liquid, supercritical, or gaseous state. Fluids, however, may also contain solids such as, for example, suspended or colloidal particles. In some embodiments, it may be advantageous to control the residence time of the fluidization fluid in the reactor. The residence time of the fluidization fluid may be defined as the volume of the reactor divided by the volumetric flow rate of the fluidization fluid. The residence time of the fluidization fluid may be at least about 0.1 second, at least about 0.2 second, at least about 0.5 second, at least about 1 second, at least about 2 seconds, at least about 3 seconds, at least about 4 seconds, at least about 5 seconds, at least about 6 seconds, at least about 8 seconds, at least about 10 seconds, at least about 12 seconds, at least about 24 seconds, or at least about 48 seconds. The residence time of the fluidization fluid may be from about 0.1 second to about 48 seconds, from about 0.2 second to about 48 seconds, from about 0.5 second to about 480 seconds, from about 1 second to about 48 seconds, from about 3 seconds to about 48 seconds, from about 5 seconds to about 48 seconds, from about 6 seconds to about 48 seconds, from about 8 seconds to about 48 seconds, from about 10 seconds to about 48 seconds, from about 12 seconds to about 48 seconds, or from about 24 seconds to about 48 seconds.

Suitable fluidization fluids that may be used in this invention include, for example, inert gases (e.g., helium, argon, neon, etc.), hydrogen, nitrogen, carbon monoxide, and carbon dioxide, among others.

As shown in the illustrative embodiment of FIG. 1A, the products (e.g., fluid hydrocarbon products) formed during the reaction of the reactants (e.g., the solid

hydrocarbonaceous material) exit the reactor via a product stream 30. In addition to the reaction products, the product stream may, in some cases, comprise unreacted reactant(s), fluidization fluid, and/or catalyst. In one set of embodiments, the desired reaction product(s) (e.g., liquid aromatic hydrocarbons, olefin hydrocarbons, gaseous products, etc.) may be recovered from an effluent stream of the reactor.

As shown in the illustrative embodiment of FIG. 1A, product stream 30 may be fed to an optional solids separator 32. The solids separator may be used, in some cases, to separate the reaction products from catalyst (e.g., at least partially deactivated catalyst) present in the product stream. In addition, the solids separator may be used, in some instances, to remove coke and/or ash from the catalyst. In some embodiments, the solids separator may comprise optional purge stream 33, which may be used to purge coke, ash, and/or catalyst from the solids separator.

The equipment required to achieve the solids separation and/or decoking steps can be readily designed by one of ordinary skill in the art. For example, the solids separator may comprise a vessel comprising a mesh material that defines a retaining portion and a permeate portion of the vessel. The mesh may serve to retain the catalyst within the retaining portion while allowing the reaction product to pass to the permeate portion. The catalyst may exit the solids separator through a port on the retaining side of the mesh while the reaction product may exit a port on the permeate side of the mesh. Other examples of solids separators and/or decokers are described in more detail in *Kirk-Othmer Encyclopedia of Chemical Technology* (Online), Vol. 11, Hoboken, N.J.: Wiley-Interscience, c2001-, pages 700-734; and C. D. Cooper and F. C. Alley. *Air Pollution Control, A Design Approach*, Second Ed. Prospect Heights, Illinois: Waveland Press, Inc. c1994, pages 127-149, which are incorporated herein by reference.

The solids separator may be operated at any suitable temperature. In some embodiments, the solids separator may be operated at elevated temperatures. For certain reactions, the use of elevated temperatures in the solids separator can allow for additional reforming and/or reaction of the compounds from the reactor. This may allow for the increased formation of desirable products. While not wishing to be bound by any theory, it is believed that elevated temperatures in the solids separator may provide enough energy to drive endothermic reforming reactions. The solids separator may be operated at a temperature of, for example, between about 25 °C and about 200 °C, between about

200 °C and about 500 °C, between about 500 °C and about 600 °C, or between about 600 °C and about 800 °C. In some cases, the solids separator may be operated at temperatures of at least about 500 °C, at least about 600 °C, at least 700 °C, at least 800 °C, or higher.

It may be beneficial to control the residence time of the catalyst in the solids separator. The residence time of the catalyst in the solids separator may be defined as the volume of the solids separator divided by the volumetric flow rate of the catalyst through the solids separator. In some cases, relatively long residence times of the catalyst in the solids separator may be desired in order to facilitate the removal of sufficient amounts of ash, coke, and/or other undesirable products from the catalyst. In addition, by employing relatively long residence times of the catalyst in the solids separator, the pyrolysis products may be further reacted to produce desirable products. The residence time and temperature in the solids separator may together be selected such that a desired product stream is produced. The residence time of the catalyst in the solids separator may be at least about 1 second, at least about 5 seconds, at least about 7 seconds, at least about 10 seconds, at least about 30 seconds, at least about 60 seconds, at least about 120 seconds, at least about 240 seconds, at least about 300 seconds, at least about 600 seconds, or at least about 1200 seconds. Methods for controlling the residence time of the catalyst in the solids separator are known by those skilled in the art. For example, in some cases, the interior wall of the solids separator may comprise baffles that serve to restrict the flow of catalyst through the solids separator and/or increase the path length of fluid flow in the solids separator. Additionally or alternatively, the residence time of the catalyst in the solids separator may be controlled by controlling the flow rate of the catalyst through the solids separator (e.g., by controlling the flow rate of the fluidizing fluid through the reactor).

The solids separator may have any suitable size. For example, the solids separator may have a volume between about 0.1-1 L, 1-50 L, 50-100 L, 100-250 L, 250-500 L, 500-1000 L, 1000-5000 L, 5000-10,000 L, or 10,000-50,000 L. In some instances, the solids separator may have a volume greater than about 1 L, or in other instances, greater than about 10 L, 50 L, 100 L, 250 L, 500 L, 1,000 L, or 10,000 L. Solids separator volumes greater than 50,000 L are also possible. The solids separator may be cylindrical, spherical, or any other shape and may be circulating or non-

circulating. In some embodiments, the solids separator may comprise a vessel or other unit operation similar to that used for one or more of the reactor(s) used in the process. The flow path for the catalyst in the solids separator may comprise any suitable geometry. For example, the flow path may be substantially straight. In some cases, the solids separator may comprise a flow channel with a serpentine, meandering, helical, or any other suitable shape. The ratio of the length of the flow path of the solids separator (or, in certain embodiments, the path length of the catalyst through the solids separator) to the average diameter of the solids separator channel may comprise any suitable ratio. The ratio may be at least about 2:1, at least 5:1, at least 10:1, at least 50:1, at least 100:1, or greater.

The solids separator may not be required in all embodiments. For example, for situations in which catalytic fixed bed reactors are employed, the catalyst may be retained within the reactor, and the reaction products may exit the reactor substantially free of catalyst, thus negating the need for a separation step.

The separated catalyst may exit the solids separator via stream 34. A portion of the separated catalyst may be returned to the reactor via a return pipe, not shown in FIG. 1A. The catalyst exiting the separator may be at least partially deactivated. The separated catalyst may be fed to a regenerator 36 in which any catalyst that was at least partially deactivated may be re-activated. The regenerator may comprise an optional purge stream 37, which may be used to purge coke, ash, and/or catalyst from the regenerator. Methods for activating catalyst are well-known to those skilled in the art, for example, as described in *Kirk-Othmer Encyclopedia of Chemical Technology* (Online), Vol. 5, Hoboken, N.J. : Wiley-Interscience, c2001-, pages 255-322, which are incorporated herein by reference.

A portion of the catalyst may be removed from the reactor through a catalyst exit port (not shown in FIG. 1A.). The catalyst removed from the reactor may be partially deactivated and passed via a conduit into regenerator 36, or into a separate regenerator (not shown in FIG. 1A). Removed catalyst that has been regenerated may be returned to the reactor via stream 47, or may be returned to the reactor separately from the fluidization gas via a separate stream (not shown in FIG. 1A.).

An oxidizing agent may be fed to the regenerator via a stream 38, e.g., as shown in FIG. 1A. The oxidizing agent may originate from any source including, for example,

a tank of oxygen, atmospheric air, steam, among others. In the regenerator, the catalyst may be re-activated by reacting the catalyst with the oxidizing agent. The deactivated catalyst may comprise residual carbon and/or coke, which may be removed via reaction with the oxidizing agent in the regenerator. The regenerator in FIG. 1A comprises a vent stream 40 which may include regeneration reaction products, residual oxidizing agent, etc.

The regenerator may be of any suitable size mentioned above in connection with the reactor or the solids separator. In addition, the regenerator may be operated at elevated temperatures in some cases (e.g., at least about 300 °C, 400 °C, 500 °C, 600 °C, 700 °C, 800 °C, or higher). The residence time of the catalyst in the regenerator may also be controlled using methods known by those skilled in the art, including those outlined above. The mass flow rate of the catalyst through the regenerator may be coupled to the flow rate(s) in the reactor and/or solids separator in order to preserve the mass balance in the system.

The regenerated catalyst may exit the regenerator via stream 42. The regenerated catalyst may be recycled back to the reactor via recycle stream 47. In some cases, catalyst may be lost from the system or removed intentionally during operation. Additional "makeup" catalyst may be added to the system via a makeup stream 46. The regenerated and makeup catalyst may be fed to the reactor with the fluidization fluid via recycle stream 47. Alternatively, the catalyst and fluidization fluid may be fed to the reactor via separate streams.

Referring back to solids separator 32 in FIG. 1A, the reaction products (e.g., fluid hydrocarbon products) may exit the solids separator via stream 48. In some cases, a fraction of stream 48 may be purged via purge stream 60. The contents of the purge stream may be fed to a combustor or a water-gas shift reactor, for example, to recuperate energy that would otherwise be lost from the system. In some cases, the reaction products in stream 48 may be fed to an optional condenser 50. The condenser may comprise a heat exchanger which condenses at least a portion of the reaction product from a gaseous to a liquid state. The condenser may be used to separate the reaction products into gaseous, liquid, and solid fractions. The operation of condensers is well known to those skilled in the art. Examples of condensers that may be used are described in more detail in *Perry's Chemical Engineers' Handbook,* Section 11: "Heat

Transfer Equipment." 8th ed. New York : McGraw-Hill, c2008, which is incorporated herein by reference.

The condenser may also make use of pressure change to condense portions of the product stream. In FIG. 1A, stream 54 may comprise the liquid fraction of the reaction products (e.g., water, aromatic compounds, olefin compounds, etc.), and stream 74 may comprise the gaseous fraction of the reaction products (e.g., CO, CO_2, H_2, etc.). In some embodiments, the gaseous fraction may be fed to a vapor recovery system 70. The vapor recovery system may be used, for example, to recover any desirable vapors within stream 74 and transport them via stream 72. In addition, stream 76 may be used to transport CO, CO_2, and/or other non-recoverable gases from the vapor recovery system. The optional vapor recovery system may be placed in other locations. For example, in some embodiments, a vapor recovery system may be positioned downstream of purge stream 54. One skilled in the art can select an appropriate placement for a vapor recovery system.

Other products (e.g., excess gas) may be transported to optional compressor 26 via stream 56, where they may be compressed and used as fluidization gas in the reactor (stream 22) and/or where they may assist in transporting the hydrocarbonaceous material to the reactor (streams 58) or may be used to transport catalyst to the reactor (not shown), or may be used to transport additional non-solid feeds to the reactor. In some instances, the liquid fraction may be further processed, for example, to separate the water phase from the organic phase, to separate individual compounds, etc.

It should be understood that, while the set of embodiments described by FIG. 1A includes a reactor, solids separator, regenerator, condenser, etc., not all embodiments will involve the use of these elements. For example, in some embodiments, the feed stream(s) may be fed to a catalytic fixed bed reactor, reacted, and the reaction products may be collected directly from the reactor and cooled without the use of a dedicated condenser. In some instances, while a dryer, grinding system, solids separator, regenerator, condenser, and/or compressor may be used as part of the process, one or more of these elements may comprise separate units not fluidically and/or integrally connected to the reactor. In other embodiments one or more of the dryer, grinding system, solids separator, regenerator, condenser, and/or compressor may be absent. In some embodiments, the desired reaction product(s) may be recovered at any point in the

production process (e.g., after passage through the reactor, after separation, after condensation, etc.).

The process may involve the use of more than one reactor. For instance, multiple reactors may be connected in fluid communication with each other, for example, to operate in series and/or in parallel, as shown in the exemplary embodiment of FIG. 1B. The process may comprise providing a solid hydrocarbonaceous material in a first reactor and pyrolyzing, within the first reactor, at least a portion of the solid hydrocarbonaceous material under reaction conditions sufficient to produce one or more pyrolysis products. A catalyst may be provided to the first reactor, and at least a portion of the one or more pyrolysis products in the first reactor may be catalytically reacted using the catalyst under reaction conditions sufficient to produce one or more fluid hydrocarbon products. The process may further comprise catalytically reacting at least a portion of the one or more pyrolysis products in a second reactor using a catalyst under reaction conditions sufficient to produce one or more fluid hydrocarbon products. After catalytically reacting at least a portion of the one or more pyrolysis products in the second reactor, the process may comprise the step of further reacting within the second reactor at least a portion of the one or more fluid hydrocarbon products from the first reactor to produce one or more other hydrocarbon products.

In FIG. 1B, the reaction product from reactor 20 may be transported to a second reactor 20'. Those skilled in the art are familiar with the use of multiple-reactor systems for the pyrolysis of organic material to produce organic products and such systems are known in the art. While FIG. 1B illustrates a set of embodiments in which the reactors are in fluid communication with each other, in some instances, the two reactors may not be in fluid communication. For example, a first reactor may be used to produce a first reaction product which may be transported to a separate facility for reaction in a second reactor. In some instances, a composition comprising a solid hydrocarbonaceous material (with or without a catalyst) may be heated in a first reactor, and at least a portion of the solid hydrocarbonaceous material may be pyrolyzed to produce a pyrolysis product (and optionally at least partially deactivated catalyst). The first pyrolysis product may be in the form of a liquid and/or a gas. The composition comprising the first pyrolysis product may then be heated in a second reactor, which may or may not be in fluid communication with the first reactor. After the heating step in the second

reactor, a second pyrolysis product from the second reactor may be collected. The second pyrolysis product may be in the form of a liquid and/or a gas. In some cases, the composition comprising hydrocarbonaceous material that is fed into the first reactor may comprise, for example, a mixture of a solid hydrocarbonaceous material and a solid catalyst. The first pyrolysis product produced from the first reactor may be different in chemical composition, amount, state (e.g., a fluid vs. a gas) than the second pyrolysis product. For example, the first pyrolysis product may substantially include a liquid, while the second pyrolysis product may substantially include a gas. In another example, the first pyrolysis product may include a fluid product (e.g., a bio-oil, sugar), and the second pyrolysis product may comprise a relatively higher amount of aromatics than the first pyrolysis product. In some instances, the first pyrolysis product may include a fluid product (e.g., including aromatic compounds), and the second pyrolysis product may comprise a relatively higher amount of olefins than the first pyrolysis product. In yet another example, the first pyrolysis product may include a fluid product (e.g., a bio-oil, sugar), and the second pyrolysis product may comprise a relatively higher amount of oxygenated aromatic compounds than the first pyrolysis product.

One or more of the reactors in a multiple reactor configuration may comprise a fluidized bed reactor (e.g., a circulating fluidized bed reactor, a turbulent fluidized bed reactor, etc.) or, in other instances, any other type of reactor (e.g., any of the reactors mentioned above). For example, the first reactor may comprise a circulating fluidized bed reactor or a turbulent fluidized bed reactor, and the second reactor comprises a circulating fluidized bed reactor or a turbulent fluidized bed reactor in fluid communication with the first reactor. In addition, the multiple reactor configuration may include any of the additional processing steps and/or equipment mentioned herein (e.g., a solids separator, a regenerator, a condenser, etc.). The reactors and/or additional processing equipment may be operated using any of the processing parameters (e.g., temperatures, residence times, etc.) mentioned herein.

Catalyst components useful in the context of this invention can be selected from any catalyst known in the art, or as would be understood by those skilled in the art made aware of this invention. Functionally, catalysts may be limited only by the capability of any such material to promote and/or effect dehydration, dehydrogenation, isomerization, hydrogen transfer, aromatization, decarbonylation, decarboxylation, aldol condensation

and/or any other reaction or process associated with or related to the pyrolysis of a hydrocarbonaceous material. Catalyst components can be considered acidic, neutral or basic, as would be understood by those skilled in the art.

The catalyst particles described herein may comprise polycrystalline solids (e.g., polycrystalline particles) in some cases. The catalyst particles may also comprise single crystals, in some embodiments. In certain cases, the particles may be distinct and separate physical objects that are stand-alone. In other cases, the particles may, at least at certain points in their preparation and/or use, comprise an agglomerate of a plurality of individual particles in intimate contact with each other.

A catalyst used in embodiments described herein (e.g., in the feed stream, in the reactor, etc.) may be of any suitable size. In some cases, it may be advantageous to use catalysts comprising relatively small catalyst particles, which may, as mentioned previously, in certain embodiments, be in the form of larger catalyst objects that may be comprised of a plurality of agglomerated catalyst particles. In some embodiments, for example, the use of small catalyst particles may increase the extent to which the hydrocarbonaceous material may contact the surface sites of the catalyst due to, for example, increased external catalytic surface area and decreased diffusion distances through the catalyst. In some cases, catalyst size and/or catalyst particle size may be chosen based at least in part on, for example, the type of fluid flow desired and the catalyst lifetime.

In some embodiments, the average diameter (as measured by conventional sieve analysis) of catalyst objects, which may in certain instances each comprise a single catalyst particle or in other instances comprise an agglomerate of a plurality of particles, may be less than about 5 mm, less than about 2 mm, less than about 1 mm, less than about 500 microns, less than about 60 mesh (250 microns), less than about 100 mesh (149 microns), less than about 140 mesh (105 microns), less than about 170 mesh (88 microns), less than about 200 mesh (74 microns), less than about 270 mesh (53 microns), or less than about 400 mesh (37 microns), or smaller.

The catalyst may comprise particles having a maximum cross-sectional dimension of less than about 5 microns, less than about 1 micron, less than about 500 nm, less than about 100 nm, between about 100 nm and about 5 microns, between about 500 nm and about 5 microns, between about 100 nm and about 1 micron, or between about 500 nm and

about 1 micron. Catalyst particles having the dimensions within the ranges noted immediately above may be agglomerated to form discrete catalyst objects having dimensions within the ranges noted above. As used here, the "maximum cross-sectional dimension" of a particle refers to the largest dimension between two boundaries of a particle. One of ordinary skill in the art would be capable of measuring the maximum cross-sectional dimension of a particle by, for example, analyzing a scanning electron micrograph (SEM) of a catalyst preparation. In embodiments comprising agglomerated particles, the particles should be considered separately when determining the maximum cross-sectional dimensions. In such a case, the measurement may be performed by establishing imaginary boundaries between each of the agglomerated particles, and measuring the maximum cross-sectional dimension of the hypothetical, individuated particles that result from establishing such boundaries. In some embodiments, a relatively large number of the particles within a catalyst may have maximum cross-sectional dimensions that lie within a given range. For example, in some embodiments, at least about 50%, at least about 75%, at least about 90%, at least about 95%, or at least about 99% of the particles within a catalyst have maximum cross-sectional dimensions of less than about 5 microns, less than about 1 micron, less than about 500 nm, less than about 100 nm, between about 100 nm and about 5 microns, between about 500 nm and about 5 microns, between about 100 nm and about 1 micron, or between about 500 nm and about 1 micron.

A relatively large percentage of the volume of the catalyst can be occupied by particles with maximum cross-sectional dimensions within a specific range, in some cases. For example, in some embodiments, at least about 50%, at least about 75%, at least about 90%, at least about 95%, or at least about 99% of the sum of the volumes of all the catalyst used is occupied by particles having maximum cross-sectional dimensions of less than about 5 microns, less than about 1 micron, less than about 500 nm, less than about 100 nm, between about 100 nm and about 5 microns, between about 500 nm and about 5 microns, between about 100 nm and about 1 micron, or between about 500 nm and about 1 micron.

In some embodiments, the particles within a catalyst may be substantially the same size. For example, the catalyst may comprise particles with a distribution of dimensions such that the standard deviation of the maximum cross-sectional dimensions

of the particles is no more than about 50%, no more than about 25%, no more than about 10%, no more than about 5%, no more than about 2%, or no more than about 1% of the average maximum cross-sectional dimensions of the particles. Standard deviation (lower-case sigma) may be calculated as:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n}(D_i - D_{avg})^2}{n-1}}$$

wherein D_i is the maximum cross-sectional dimension of particle i, D_{avg} is the average of the maximum cross-sectional dimensions of all the particles, and n is the number of particles within the catalyst. The percentage comparisons between the standard deviation and the average maximum cross-sectional dimensions of the particles outlined above can be obtained by dividing the standard deviation by the average and multiplying by 100%.

Using catalysts including particles within a chosen size distribution indicated above can lead to an increase in the yield and/or selectivity of aromatic compounds produced by the reaction of the hydrocarbonaceous material. For example, in some cases, using catalysts containing particles with a desired size range (e.g., any of the size distributions outlined above) can result in an increase in the amount of aromatic compounds in the reaction product of at least about 5%, at least about 10%, or at least about 20%, relative to an amount of aromatic compounds that would be produced using catalysts containing particles with a size distribution outside the desired range (e.g., with a large percentage of particles larger than 1 micron, larger than 5 microns. etc.).

Alternatively, catalysts may be selected according to pore size (e.g., mesoporous and pore sizes typically associated with zeolites), e.g., average pore sizes of less than about 100 Angstroms, less than about 50 Angstroms, less than about 20 Angstroms, less than about 10 Angstroms, less than about 5 Angstroms, or smaller. In some embodiments, catalysts with average pore sizes of from about 5 Angstroms to about 100 Angstroms may be used. In some embodiments, catalysts with average pore sizes of between about 5.5 Angstroms and about 6.5 Angstroms, or between about 5.9 Angstroms and about 6.3 Angstroms may be used. In some cases, catalysts with average pore sizes of between about 7 Angstroms and about 8 Angstroms, or between about 7.2 Angstroms and about 7.8 Angstroms may be used.

As used herein, the term "pore size" is used to refer to the smallest cross-sectional diameter of a pore. The smallest cross-sectional diameter of a pore may correspond to the smallest cross-sectional dimension (e.g., a cross-sectional diameter) as measured perpendicularly to the length of the pore. In some embodiments, a catalyst with an "average pore size" or a "pore size distribution" of X refers to a catalyst in which the average of the smallest cross-sectional diameters of the pores within the catalyst is about X. It should be understood that "pore size" or "smallest cross sectional diameter" of a pore as used herein refers to the Norman radii adjusted pore size well known to those skilled in the art. Determination of Norman radii adjusted pore size is described, for example, in Cook, M.; Conner, W. C., "How big are the pores of zeolites?" Proceedings of the International Zeolite Conference, 12th, Baltimore, July 5-10, 1998; (1999), 1, pp 409-414, which is incorporated herein by reference in its entirety. As a specific exemplary calculation, the atomic radii for ZSM-5 pores are about 5.5-5.6 Angstroms, as measured by x-ray diffraction. In order to adjust for the repulsive effects between the oxygen atoms in the catalyst, Cook and Conner have shown that the Norman adjusted radii are 0.7 Angstroms larger than the atomic radii (about 6.2-6.3 Angstroms).

One of ordinary skill in the art will understand how to determine the pore size (e.g., minimum pore size, average of minimum pore sizes) in a catalyst. For example, x-ray diffraction (XRD) can be used to determine atomic coordinates. XRD techniques for the determination of pore size are described, for example, in Pecharsky, V.K. et al, "Fundamentals of Powder Diffraction and Structural Characterization of Materials," Springer Science+Business Media, Inc., New York, 2005, incorporated herein by reference in its entirety. Other techniques that may be useful in determining pore sizes (e.g., zeolite pore sizes) include, for example, helium pycnometry or low pressure argon adsorption techniques. These and other techniques are described in Magee, J.S. et al, "Fluid Catalytic Cracking: Science and Technology," Elsevier Publishing Company, July 1, 1993, pp. 185-195, which is incorporated herein by reference in its entirety. Pore sizes of mesoporous catalysts may be determined using, for example, nitrogen adsorption techniques, as described in Gregg, S. J. at al, "Adsorption, Surface Area and Porosity," 2nd Ed., Academic Press Inc., New York, 1982 and Rouquerol, F. et al, "Adsorption by powders and porous materials. Principles, Methodology and Applications," Academic Press Inc., New York, 1998, both incorporated herein by reference in their entirety.

Unless otherwise indicated, pore sizes referred to herein are those determined by x-ray diffraction corrected as described above to reflect their Norman radii adjusted pore sizes.

A screening method may be used to select catalysts with appropriate pore sizes for the conversion of specific pyrolysis product molecules. The screening method may comprise determining the size of pyrolysis product molecules desired to be catalytically reacted (e.g., the molecule kinetic diameters of the pyrolysis product molecules). One of ordinary skill in the art can calculate, for example, the kinetic diameter of a given molecule. The type of catalyst may then be chosen such that the pores of the catalyst (e.g., Norman adjusted minimum radii) are sufficiently large to allow the pyrolysis product molecules to diffuse into and/or react with the catalyst. In some embodiments, the catalysts are chosen such that their pore sizes are sufficiently small to prevent entry and/or reaction of pyrolysis products whose reaction would be undesirable.

The catalyst may be selected from naturally-occurring zeolites, synthetic zeolites and combinations thereof. The catalyst may be a Mordenite Framework Inverted (MFI) type zeolite catalyst, such as a ZSM-5 zeolite catalyst. Catalysts comprising ZSM-5 that may be used with or without modification are available commercially. The catalysts that are provided for herein may comprise acid or catalytically active sites. While not wishing to be bound by theory, it is believed that various acid sites in ZSM-5 and other zeolites are catalytically active for reactions of the hydrocarbonaceous materials including dehydration, decarbonylation, decarboxylation, isomerization, oligomerization and/or dehydrogenation, hence the terms “acid sites” and “catalytically active sites” may be used interchangeably. Other types of useful zeolite catalysts may include ferrierite, zeolite Y, zeolite beta, modernite, MCM-22, ZSM-23, ZSM-57, SUZ-4, EU-1, ZSM-11, (S)AlPO-31, SSZ-23, mixtures of two or more thereof, and the like.

The catalyst may comprise, in addition to alumina and silica, one or more additional metals and/or a metal oxides. Suitable metals and/or oxides may include, for example, nickel, platinum, vanadium, palladium, manganese, cobalt, zinc, copper, chromium, gallium, and/or any of their oxides, among others. The metal and/or metal oxide can be impregnated into the catalyst (e.g., in the interstices of the lattice structure of the catalyst), in some embodiments. The metal or metal oxide can be added to the zeolite by any of a number of techniques known to those skilled in the art, such as, but not limited to, impregnation, ion exchange, vapor deposition, and the like. The zeolite may

comprise small amounts of structure stabilizing elements such as phosphorus, lanthanum, rare earths, and the like, typically at levels that are less than about 1 % by weight of the zeolite. The catalyst may be conditioned before operation in the process by a wide range of techniques known to those skilled in the art such as, but not limited to, oxidation, calcination, reduction, cyclic oxidation and reduction, steaming, hydrolysis, and the like. The metal and/or metal oxide may be incorporated into the lattice structure of the catalyst. For example, the metal and/or metal oxide may be included during the preparation of the catalyst, and the metal and/or metal oxide may occupy a lattice site of the resulting catalyst (e.g., a zeolite catalyst). As another example, the metal and/or metal oxide may react or otherwise interact with a zeolite such that the metal and/or metal oxide displaces an atom within the lattice structure of the zeolite.

In certain embodiments, a Mordenite Framework Inverted (MFI) zeolite catalyst comprising gallium may be used. For example, a galloaluminosilicate MFI (GaAlMFI) zeolite catalyst may be used. One of ordinary skill in the art would be familiar with GaAlMFI zeolites, which may be thought of as aluminosilicate MFI zeolites in which some of the Al atoms have been replaced with Ga atoms. In some instances, the zeolite catalyst may be in the hydrogen form (e.g., H-GaAlMFI). The galloaluminosilicate MFI catalyst may be a ZSM-5 zeolite catalyst in which some of the aluminum atoms have been replaced with gallium atoms, in some embodiments.

In some instances, the ratio of moles of Si in the galloaluminosilicate zeolite catalyst to the sum of the moles of Ga and Al (i.e., the molar ratio expressed as Si:(Ga+Al)) in the galloaluminosilicate zeolite catalyst may be at least about 15:1, at least about 20:1, at least about 25:1, at least about 35:1, at least about 50:1, at least about 75:1, or higher. In some embodiments, it may be advantageous to employ a catalyst with a ratio of moles of Si in the zeolite to the sum of the moles of Ga and Al of between about 15:1 and about 100:1, from about 15:1 to about 75:1, between about 25:1 and about 80:1, or between about 50:1 and about 75:1. In some instances, the ratio of moles of Si in the galloaluminosilicate zeolite catalyst to the moles of Ga in the galloaluminosilicate zeolite catalyst may be at least about 30:1, at least about 60:1, at least about 120:1, at least about 200:1, between about 30:1 and about 300:1, between about 30:1 and about 200:1, between about 30:1 and about 120:1, or between about 30:1 and about 75:1. The ratio of the moles of Si in the galloaluminosilicate zeolite catalyst to the moles of Al in the

galloaluminosilicate zeolite catalyst may be at least about 10:1, at least about 20:1, at least about 30:1, at least about 40:1, at least about 50:1, at least about 75:1, between about 10:1 and about 100:1, between about 10:1 and about 75:1, between about 10:1 and about 50:1, between about 10:1 and about 40:1, or between about 10:1 and about 30:1.

In addition, in some cases, properties of the catalysts (e.g., pore structure, type and/or number of acid sites, etc.) may be chosen to selectively produce a desired product.

It may be desirable, in some embodiments, to employ one or more catalysts to establish a bimodal distribution of pore sizes. In some cases, a single catalyst with a bimodal distribution of pore sizes may be used (e.g., a single catalyst that contains predominantly 5.9-6.3 Angstrom pores and 7-8 Angstrom pores). In other cases, a mixture of two or more catalysts may be employed to establish the bimodal distribution (e.g., a mixture of two catalysts, each catalyst type including a distinct range of average pore sizes). In some embodiments, one of the one or more catalysts comprises a zeolite catalyst and another of the one or more catalysts comprises a non-zeolite catalyst (e.g., a mesoporous catalyst, a metal oxide catalyst, etc.).

For example, in some embodiments at least about 70%, at least about 80%, at least about 90%, at least about 95%, at least about 98%, or at least about 99% of the pores of the one or more catalysts (e.g., a zeolite catalyst, a mesoporous catalyst, etc.) have smallest cross-sectional diameters that lie within a first size distribution or a second size distribution. In some cases, at least about 2%, at least about 5%, or at least about 10% of the pores of the one or more catalysts have smallest cross-sectional diameters that lie within the first size distribution; and at least about 2%, at least about 5%, or at least about 10% of the pores of the one or more catalysts have smallest cross-sectional diameters that lie within the second size distribution. In some cases, the first and second size distributions are selected from the ranges provided above. In certain embodiments, the first and second size distributions are different from each other and do not overlap. An example of a non-overlapping range is 5.9-6.3 Angstroms and 6.9-8.0 Angstroms, and an example of an overlapping range is 5.9-6.3 Angstroms and 6.1-6.5 Angstroms. The first and second size distributions may be selected such that the range are not immediately adjacent one another, an example being pore sizes of 5.9-6.3 Angstroms and 6.9-8.0 Angstroms. An example of a range that is immediately adjacent one another is pore sizes of 5.9-6.3 Angstroms and 6.3-6.7 Angstroms.

As a specific example, in some embodiments one or more catalysts is used to provide a bimodal pore size distribution for the simultaneous production of aromatic and olefin compounds. That is, one pore size distribution may advantageously produce a relatively high amount of aromatic compounds, and the other pore size distribution may advantageously produce a relatively high amount of olefin compounds. In some embodiments, at least about 70%, at least about 80%, at least about 90%, at least about 95%, at least about 98%, or at least about 99% of the pores of the one or more catalysts have smallest cross-sectional diameters between about 5.9 Angstroms and about 6.3 Angstroms or between about 7 Angstroms and about 8 Angstroms. In addition, at least about 2%, at least about 5%, or at least about 10% of the pores of the one or more catalysts have smallest cross-sectional diameters between about 5.9 Angstroms and about 6.3 Angstroms; and at least about 2%, at least about 5%, or at least about 10% of the pores of the one or more catalysts have smallest cross-sectional diameters between about 7 Angstroms and about 8 Angstroms.

In some embodiments, at least about 70%, at least about 80%, at least about 90%, at least about 95%, at least about 98%, or at least about 99% of the pores of the one or more catalysts have smallest cross-sectional diameters between about 5.9 Angstroms and about 6.3 Angstroms or between about 7 Angstroms and about 200 Angstroms. In addition, at least about 2%, at least about 5%, or at least about 10% of the pores of the one or more catalysts have smallest cross-sectional diameters between about 5.9 Angstroms and about 6.3 Angstroms; and at least about 2%, at least about 5%, or at least about 10% of the pores of the one or more catalysts have smallest cross-sectional diameters between about 7 Angstroms and about 200 Angstroms.

In some embodiments, at least about 70%, at least about 80%, at least about 90%, at least about 95%, at least about 98%, or at least about 99% of the pores of the one or more catalysts have smallest cross-sectional diameters that lie within a first distribution and a second distribution, wherein the first distribution is between about 5.9 Angstroms and about 6.3 Angstroms and the second distribution is different from and does not overlap with the first distribution. In some embodiments, the second pore size distribution may be between about 7 Angstroms and about 200 Angstroms, between about 7 Angstroms and about 100 Angstroms, between about 7 Angstroms and about 50 Angstroms, or between about 100 Angstroms and about 200 Angstroms. In some

embodiments, the second catalyst may be mesoporous (e.g., have a pore size distribution of between about 2 nm and about 50 nm).

In some embodiments, the bimodal distribution of pore sizes may be beneficial in reacting two or more hydrocarbonaceous feed material components. For example, some embodiments comprise providing a solid hydrocarbonaceous material comprising a first component and a second component in a reactor, wherein the first and second components are different. Examples of compounds that may be used as first or second components include any of the hydrocarbonaceous materials described herein (e.g., sugar cane bagasse, glucose, wood, corn stover, cellulose, hemi-cellulose, lignin, or any others). For example, the first component may comprise one of cellulose, hemi-cellulose and lignin, and the second component comprises one of cellulose, hemicellulose and lignin. The method may further comprise providing first and second catalysts in the reactor. In some embodiments, the first catalyst may have a first pore size distribution and the second catalyst may have a second pore size distribution, wherein the first and second pore size distributions are different and do not overlap. The first pore size distribution may be, for example, between about 5.9 Angstroms and about 6.3 Angstroms. The second pore size distribution may be, for example, between about 7 Angstroms and about 200 Angstroms, between about 7 Angstroms and about 100 Angstroms, between about 7 Angstroms and about 50 Angstroms, or between about 100 Angstroms and about 200 Angstroms. In some cases, the second catalyst may be mesoporous or non-porous.

The first catalyst may be selective for catalytically reacting the first component or a derivative thereof to produce a fluid hydrocarbon product. In addition, the second catalyst may be selective for catalytically reacting the second component or a derivative thereof to produce a fluid hydrocarbon product. The method may further comprise pyrolyzing within the reactor at least a portion of the hydrocarbonaceous material under reaction conditions sufficient to produce one or more pyrolysis products and catalytically reacting at least a portion of the pyrolysis products with the first and second catalysts to produce the one or more hydrocarbon products. In some instances, at least partially deactivated catalyst may also be used.

In certain embodiments, a method used in combination with embodiments described herein includes increasing the catalyst to hydrocarbonaceous material mass ratio

of a composition to increase production of identifiable aromatic compounds. As illustrated herein, representing but one distinction over certain prior catalytic pyrolysis methods, articles and methods described herein can be used to produce discrete, identifiable aromatic, biofuel compounds selected from but not limited to benzene, toluene, propylbenzene, ethylbenzene, methylbenzene, methylethylbenzene, trimethylbenzene, xylenes, indanes, naphthalene, methylnaphthelene, dimethylnaphthalene, ethylnaphthalene, hydrindene, methylhydrindene, and dimethylhydrindene and combinations thereof.

In some embodiments, the reaction chemistry of a catalyst may be affected by adding one or more additional compounds. For example, the addition of a metal to a catalyst may result in a shift in selective formation of specific compounds (e.g., addition of metal to alumina-silicate catalysts may result in the production of more CO). In addition, when the fluidization fluid comprises hydrogen, the amount of coke formed on the catalyst may be decreased.

The catalyst may comprise both silica and alumina. The silica (SiO_2) and alumina (Al_2O_3) in the catalyst may be present in any suitable molar ratio. For example, in some cases, the catalyst in the feed may comprise a silica (SiO_2) to alumina (Al_2O_3) molar ratio of between about 10:1 and about 50:1, between about 10:1 and about 40:1, or between about 10:1 and about 20:1, or about 15:1.

In some embodiments, catalyst and hydrocarbonaceous material may be present in any suitable ratio. For example, the catalyst and hydrocarbonaceous material may be present in any suitable mass ratio in cases where the feed composition (e.g., through one or more feed streams comprising catalyst and hydrocarbonaceous material or through separate catalyst and hydrocarbonaceous material feed streams), comprises catalyst and hydrocarbonaceous material (e.g., circulating fluidized bed reactors). As another example, in cases where the reactor is initially loaded with a mixture of catalyst and hydrocarbonaceous material (e.g., a batch reactor), the catalyst and hydrocarbonaceous material may be present in any suitable mass ratio. In some embodiments involving circulating fluidized bed reactors, the mass ratio of the catalyst to hydrocarbonaceous material in the feed stream – i.e., in a composition comprising a catalyst and a hydrocarbonaceous material provided to a reactor – may be at least about 0.5:1, at least about 1:1, at least about 2:1, at least about 5:1, at least about 10:1, at least about 15:1, at least about 20:1, or higher. In some embodiments involving circulating fluidized bed

reactors, the mass ratio of the catalyst to hydrocarbonaceous material in the feed stream may be less than about 0.5:1, less than about 1:1, less than about 2:1, less than about 5:1, less than about 10:1, less than about 15:1, or less than about 20:1; or from about 0.5:1 to about 20:1, from about 1:1 to about 20:1, or from about 5:1 to about 20:1. Employing a relatively high catalyst to hydrocarbonaceous material mass ratio may facilitate introduction of the volatile organic compounds, formed from the pyrolysis of the feed material, into the catalyst before they thermally decompose to coke. Not wishing to be bound by any theory, this effect may be at least partially due to the presence of a stoichiometric excess of catalyst sites within the reactor.

In some embodiments, the articles and methods described herein may be configured to selectively produce aromatic compounds (e.g., p-xylene) in a single-stage, or alternatively, a multi-stage pyrolysis apparatus. For example, in some embodiments, the mass yield of the aromatic compounds in the fluid hydrocarbon product may be at least about 18 wt%, at least about 20 wt%, at least about 25 wt%, at least about 30 wt%, at least about 35 wt%, at least about 39 wt%, between about 18 wt% and about 40 wt%, between about 18 wt% and about 35 wt%, between about 20 wt% and about 40 wt%, between about 20 wt% and about 35 wt%, between about 25 wt% and about 40 wt%, between about 25 wt% and about 35 wt%, between about 30 wt% and about 40 wt%, or between about 30 wt% and about 35 wt%. The mass yield of p-xylene may be at least about 1.5% by weight, or at least about 2% by weight, or at least about 2.5% by weight, or at least about 3% by weight.

As used herein, the "mass yield" of aromatic compounds or p-xylene in a given product is calculated as the total weight of the aromatic compounds or p-xylene present in the fluid hydrocarbon product divided by the weight of the solid hydrocarbonaceous material used in forming the reaction product, multiplied by 100%.

As used herein, the term "aromatic compound" is used to refer to a hydrocarbon compound comprising one or more aromatic groups such as, for example, single aromatic ring systems (e.g., benzyl, phenyl, etc.) and fused polycyclic aromatic ring systems (e.g. naphthyl, 1,2,3,4-tetrahydronaphthyl, etc.). Examples of aromatic compounds include, but are not limited to, benzene, toluene, indane, indene, 2-ehtyl toluene, 3-ethyl toluene, 4-ethyl toluene, trimethyl benzene (e.g., 1,3,5-trimethyl benzene, 1,2,4-trimethyl benzene, 1,2,3- trimethyl benzene, etc.), ethylbenzene,

methylbenzene, propylbenzene, xylenes (e.g., p-xylene, m-xylene, o-xylene, etc.), naphthalene, methyl-naphthalene (e.g., 1-methyl naphthalene, anthracene, 9.10-dimethylanthracene, pyrene, phenanthrene, dimethyl-naphthalene (e.g., 1,5-dimethylnaphthalene, 1,6-dimethylnaphthalene, 2,5-dimethylnaphthalene, etc.) , ethyl-naphthalene, hydrindene, methyl-hydrindene, and dymethyl-hydrindene. Single ring and/or higher ring aromatics may be produced in some embodiments. The aromatic compounds may have carbon numbers from, for example, C_5-C_{14}, C_6-C_8, C_6-C_{12}, C_8-C_{12}, C_{10}-C_{14}.

In some embodiments, aromatic compounds (especially p-xylene) may be selectively produced when the mass-normalized space velocity of the solid hydrocarbonaceous material fed to the reactor is up to about 3 $hour^{-1}$, or up to about 2 $hour^{-1}$, or up to about 1.5 $hour^{-1}$, or up to about 0.9 $hour^{-1}$, or in the range from about 0.01 $hour^{-1}$ to about 3 $hour^{-1}$, or in the range from about 0.01 to about 2 $hour^{-1}$, or in the range from about 0.01 to about 1.5 $hour^{-1}$, or in the range from about 0.01 to about 0.9 $hour^{-1}$, or in the range from about 0.01 $hour^{-1}$ to about 0.5 $hour^{-1}$, or in the range from about 0.1 $hour^{-1}$ to about 0.9 $hour^{-1}$, or in the range from about 0.1 $hour^{-1}$ to about 0.5 $hour^{-1}$. In some instances, aromatic compounds (especially p-xylene) may be selectively produced when the reactor is operated at a temperature of between about 400 °C and about 600 °C (or between about 425 °C and about 500 °C, or between about 440 °C and about 460 °C). In addition, certain heating rates (e.g., at least about 50 °C/s, or at least about 400 °C/s), high catalyst-to-feed mass ratios (e.g., at least about 5:1), and/or high silica to alumina molar ratios in the catalyst (e.g., at least about 30:1) may be used to facilitate selective production of aromatic compounds (especially p-xylene). Some such and other process conditions may be combined with a particular reactor type, such as a fluidized bed reactor (e.g., a circulating fluidized bed reactor), to selectively produce aromatic and/or olefin compounds.

Furthermore, in some embodiments, the catalyst may be chosen to facilitate selective production of aromatic products (especially p-xylene). For example, ZSM-5 may, in some cases, preferentially produce relatively higher amounts of aromatic compounds. In some cases, catalysts that include Bronsted acid sites may facilitate selective production of aromatic compounds. In addition, catalysts with well-ordered pore structures may facilitate selective production of aromatic compounds. For example,

in some embodiments, catalysts with average pore diameters between about 5.9 Angstroms and about 6.3 Angstroms may be particularly useful in producing aromatic compounds. In addition, catalysts with average pore diameters between about 7 Angstroms and about 8 Angstroms may be useful in producing olefins. In some embodiments, a combination of one or more of the above process parameters may be employed to facilitate selective production of aromatic and/or olefin compounds. The ratio of aromatics to olefins produced may be, for example, between about 0.1:1 and about 10:1, between about 0.2:1 and about 5:1, between about 0.5:1 and about 2:1, between about 0.1:1 and about 0.5:1, between about 0.5:1 and about 1:1, between about 1:1 and about 5:1, or between about 5:1 and about 10:1.

In some embodiments, the catalyst to hydrocarbonaceous material mass ratio in the feed is adjusted to produce desirable products and/or favorable yields. As such, the catalyst to hydrocarbonaceous material mass ratio may be, for example, at least about 0.5:1, at least about 1:1, at least about 2:1, at least about 5:1, at least about 10:1, at least about 15:1, at least about 20:1, or higher in some embodiments; or, less than about 0.5:1, less than about 1:1, less than about 2:1, less than about 5:1, less than about 10:1, less than about 15:1, or less than about 20:1 in other embodiments.

Furthermore, processes described herein may result in lower coke formation than certain existing methods. For example, in some embodiments, a pyrolysis product can be formed with less than about 30 wt%, less than about 25 wt%, less than about 20 wt%, than about 15 wt%, or less than about 10 wt% of the pyrolysis product being coke. The amount of coke formed is measured as the weight of coke formed in the system divided by the weight of hydrocarbonaceous material used in forming the pyrolysis product.

The following non-limiting examples are intended to illustrate various aspects and features of the invention.

EXAMPLE

A series of zeolite catalysts are prepared and used in CFP processes for converting furan, 2-methylfuran (2MF), and pinewood, to fluid hydrocarbon products.

Catalysts

Four catalysts identified as ZSM, GaZSM, SD and GaSD are used. ZSM, which is ZSM-5, (Si/Al = 15). GaZSM is made using ion exchange, where 1 g of ZSM is refluxed in 100 mL of an aqueous solution of $Ga(NO_3)_3$ (0.01 M) at 70°C for 12 h. After

ion exchange, the solution is dried at 110°C to form a dry powder. The dry powder is calcined under air at 550°C. SD is spray-dried HZSM-5. GaSD is made by incipient wetness impregnation of SD using a $Ga(NO_3)_3$ solution (0.43 M). The impregnated GaSD is dried at 110°C and calcined under air at 550°C. The Ga content for GaZSM and GaSD is determined by inductively coupled plasma (ICP) analysis.

Chemical liquid deposition (CLD) employing tetraethylorthosilicate (TEOS) is used to modify the catalysts and thereby reduce their pore-mouth opening sizes. 1 g of catalyst is dispersed in 25 mL of hexanes. Then 0.15 mL of TEOS is added. The mixture is refluxed at 90°C for 1 h with stirring. The catalyst is recovered by centrifuge. The catalyst is dried at 100°C for 2 h and calcined at 500°C for 4 h in dry air. The pore mouth modification process is repeated two more times. The pore mouth modified catalysts may be referred to as "silylated" catalysts and are identified below with "*," for example, ZSM*, GaZSM* and GaSD*. The modification process may be referred to as a TEOS CLD silyation process.

The catalyst samples are analyzed by temperature programmed desorption of isopropyl amine (IPA) or 2,4,6-collidine (2,4,6-trimethylpyridine). Before adsorption, the sample is degassed for 2 h at 823°K. After cooling the sample to 393°K, it is exposed for 1 h to He that had been saturated with isopropylamine or 2,4,6-collidine at room temperature by flowing pure He through a bubbler containing the amine. Then the sample is held at 393°K with He flow for 2 h to remove physisorbed IPA or 2,4,6-collidine.The sample is heated to 973°K at 10°K/min. The total amount of amine desorbed is used to calculate the total number of acid sites, and the amount of amine that desorbs between about 580°K and 650°K is used to calculate the number of Bronsted acid sites for each catalyst. Due to the size of 2,4,6-collidine, it does not enter ZSM-5 pores. Therefore, desorption of 2,4,6-collidine only detects acid sites on the external surface of the catalyst or in the pores near the pore mouth openings. The IPA desorption detects acid sites within the zeolite pores as well as the acid sites on the external surface of the catalyst or in the pores near the pore mouth openings. The decrease in the 2,4,6-collidine adsorption that occurs with the sylilation treatment shows the decrease in the number of acid sites on the external surface and in or near the pore mouth openings. The decrease in these external sites is believed to be a factor in the production of m- and o-

xylene and in reducing the re-equilibration of p-xylene formed in the pores to m- or o-xylene, and thus improving the selectivity to p-xylene.

Table 1. Acid concentrations obtained by 2,4,6-collidine (kinetic diameter = 7.4 Angstroms) and isopropylamine (IPA, kinetic diameter = 5.2 Angstroms) temperature programmed desorption analysis.

Adsorbent	Collidine	Collidine	Collidine	Collidine	IPA	IPA	IPA	IPA
Catalyst	ZSM-5	ZSM-5	Ga-ZSM-5	Ga-ZSM-5	ZSM-5	ZSM-5	GaZSM--5	GaZSM--5
Acids	Total	Brønsted	Total	Brønsted	Total	Brønsted	Total	Brønsted
Before silylation	0.096	0.0548	0.051	0.0311	1.396	0.651	1.015	0.557
After silylation	0.041	0.0344	0.032	0.0265	0.706	0.413	0.676	0.335
Reduction (%)	57	37	37	15	49	37	33	40

Catalytic Conversion of Furan and 2MF

The catalytic reactions are carried out in a fixed-bed quartz reactor of 0.5 inch (1.27 cm) O.D. The catalyst, which is in the form of a fixed-bed of particulate solids, is held in the reactor by a quartz frit. The catalyst bed is calcined at a temperature of 600°C with air flowing at a rate of 60 mL/min. After calcination the reactor is purged by helium at 408 mL/min for 5 min. Furan is pumped into the helium stream using a syringe pump. Prior to the test run, the furan bypasses the reactor for 30 min. The helium stream containing the furan is then switched to go through the reactor. An air bath condenser is used to trap the heavy products. Gas phase products are collected by air bags. All runs are conducted at atmospheric pressure. No pressure drop is detected across the catalyst bed. After the reaction process is completed, the reactor is purged by helium at a flow rate of 408 mL/min for 45 seconds at the reaction temperature. The effluent is collected using air bags. After each reaction is completed, spent catalyst is regenerated at a temperature of 600°C using air at a flow rate of 60 mL/min. CO formed during regeneration is converted to CO_2 by a copper converter (copper oxide) at a temperature of 240°C. CO_2 is trapped by a CO_2 trap. Coke yield is determined by measuring the weight change of the CO_2 trap. Gas products are identified by GC-MS (Shimadzu-2010) and quantified by GC-FID/TCD (Shimadzu 2014 for gas samples, and HP-7890 for liquid samples). All hydrocarbons in the gas phase products are quantified by the GC-FID. The CO and CO_2 in the gas phase products are quantified by the GC-TCD. The GC-

FID is calibrated by C_2 – C_6 normal olefins standards (Scott Specialty Gas, 1000 ppm for each olefin), furan, benzene, toluene, xylenes (gas phase standards are prepared for these aromatics that can vaporize at room temperature), ethylbenzene, styrene, indene, naphthalene, and benzofuran. The sensitivity of a hydrocarbon is assumed to be proportional to the number of carbon molecules with similar structure (e.g. styrene vs. methylstyrenes; indene vs. methylindenes). The GC-TCD is calibrated by CO and CO_2 standards (Airgas, 6% CO_2 and 14% CO, balanced by helium). Less than 0.05% carbon or the products are collected in the condenser. A majority of the products are in either the gas phase or coke deposited on the catalyst. Carbon balances close with > 90% for all runs.

The reaction conditions for the furan conversion are a temperature of 550 °C, space velocity (WHSV) of 10.2 h^{-1}, and a partial pressure of 6 torr. The furan is pumped with a pumping rate 0.58 mL/h, and the carrier gas is maintained at 408 mL/min. The amount of catalyst that is loaded into the reactor is 53 mg.

The reaction process for 2MF is the same as the process for furan, except that 2% propylene (1.986% propylene balanced by helium) rather than pure helium is used as the carrier gas. The reaction conditions for 2MF conversion are 600°C, WHSV of 5.7 h^{-1}, and partial pressure of 4.9 torr. 2MF is pumped with a pumping rate 0.57 mL/min, and the flow of the carrier gas is maintained at 408 mL/min. The amount of catalyst that is loaded into the reactor is 92 mg.

The results are shown in Table 2.

Table 2. Summary of furan and 2MF conversions over ZSM, ZSM*, GaZSM, GaZSM* and GaSD*

Feedstock	2MF	2MF	2MF	2MF	Furan	Furan	Furan	Furan	Furan
Carrier gas	2% propylene	2% propylene	2% propylene	2% propylene	He	He	He	He	He
Catalyst	ZSM	ZSM*	GaZSM	GaZSM*	ZSM	ZSM*	GaZSM	GaZSM*	GaSD*
Temperature (°C)	600	600	600	600	550	550	550	550	550
Furan/2MF WHSV (h^{-1})	5.7	5.7	5.7	5.7	10.2	10.2	10.2	10.2	10.2
$P_{furan/2MF}$ (torr)	4.9	4.9	4.9	4.9	6.0	6.0	6.0	6.0	6.0
Olefins/furans molar ratio	3.09	3.09	3.09	3.09	–	–	–	–	–
Furan/2MF conversion (%)	99	89	98	74	33	32	41	24	24
Propylene conversion (%)	31	22	31	21	–	–	–	–	–
Overall selectivity (%)									
CO	5.9	6.6	6.0	9.7	13.1	9.3	13.9	9.5	10.6
CO_2	0.1	0.5	0.7	0.5	1.6	3.4	2.0	1.6	2.7
Methane	0.0	0.7	1.0	0.4	0.0	0.0	0.0	0.0	0.0
Olefins	27.8	27.6	18.4	32.0	14.3	17.0	12.0	11.9	16.3

Aromatics	59.6	53.3	68.5	32.4	37.4	39.0	42.7	47.7	49.3
Coke	6.2	9.4	4.7	13.6	28.5	23.3	23.9	22.8	16.3
Oxygenates	0.4	1.7	0.7	11.5	5.1	7.9	5.5	6.5	4.8
p-Xylene	5.1	14.9	6.6	4.6	1.0	1.9	0.9	1.2	3.7
Aromatic selectivity (%)									
Benzene	24.4	20.8	34.4	32.7	18.0	17.7	26.7	24.9	19.2
Toluene	28.6	23.6	34.4	35.0	20.2	19.5	17.6	15.2	20.8
Xylene	26.9	30.3	16.5	14.7	5.1	5.6	3.5	2.7	8.5
Alkylbenzenes[a]	4.0	10.4	3.5	2.7	1.5	1.7	0.9	0.5	1.6
Styrenes[b]	2.6	4.8	5.0	4.3	7.8	7.7	8.6	5.9	7.3
Indenes[c]	10.2	7.9	3.6	3.5	23.7	19.7	23.5	10.1	14.6
Naphthalenes[d]	3.2	2.4	2.7	7.1	23.8	28.2	19.2	40.8	28.0
Olefin selectivity (%)									
Ethylene	61.6	35.6	55.8	49.6	37.6	26.0	43.1	36.1	33.5
Propylene	–	–	–	–	37.8	44.5	43.6	34.0	39.7
C_4 olefins	28.0	36.7	26.8	30.3	4.5	6.2	4.0	5.0	5.6
Allene	0.1	0.5	0.7	1.0	3.7	4.1	3.1	9.8	5.7
C_5 olefins	7.3	16.3	14.2	15.0	10.8	11.2	4.7	11.0	9.4
C_6 olefins	3.0	8.9	2.0	3.7	5.5	8.0	1.5	4.1	6.1
C_7 olefins	0.0	2.0	0.5	0.3	0.0	0.0	0.0	0.0	0.0
Xylenes distribution (%)									
p-Xylene	32	92	58	96	53	89	57	96	87
m-Xylene	49	6	34	3	38	9	35	3	10
o-Xylene	19	2	9	1	10	2	8	1	3

a: Ethylbenzene and trimethylbenzene
b: Styrene and methylstyrenes
c: Indene, methylindenes, and indane
d: Naphthalene, methylnaphthalene, and dihydronaphthalene

Figures A and B show overall *p*-xylene selectivity and xylenes distribution, obtained from the conversions of 2MF and furan, respectively. In Figure A the overall *p*-xylene carbon selectivity obtained from ZSM is 5%. This value is increased to 15% by using ZSM*. The silylation dramatically increases the *para* selectivity from 32% to 92%. Similarly, the silylated GaZSM* also shows a significant increase of *para* selectivity from 58% (GaZSM) to 96%. However, the overall *p*-xylene selectivity for GaZSM* is lower than GaZSM. Table 2 shows that the conversion of 2MF for GaZSM* (74%) is lower than that for GaZSM (98%). In addition, the 2MF conversion for ZSM* (89%) is also lower than that for ZSM (99%). The decrease of activity is believed to be due to some active sites in the external surface and in the surface near pore-openings being eliminated by silica deposition. Ga deposited on ZSM may have the ability to increase overall aromatics selectivity. This is also shown in Table 2 (2MF + propylene) where the aromatics selectivity is 60% for ZSM and 69% for GaZSM. However, deactivation caused by silylation on GaZSM* may be more severe than with ZSM*, according to 2MF conversion, suggesting that some active Ga species may be located at these surfaces

and may be killed by silylation. These Ga species imposes space confinement that causes an increase of *para* selectivity (Figure A, 58% for GaZSM and 32% for ZSM). The silylation of GaZSM further imposes more space confinement and thus, gives a better *para* selectivity (96%).

For furan conversion (Figure B), increases of overall *p*-xylene selectivity and amongst xylene species towards *para* are observed from silylated catalysts. The *para* selectivity is increased from 53% for ZSM to 89% for ZSM*, and from 57% for GaZSM to 96% for GaZSM*. Silylation also causes the activity to decrease as shown in Table 1 where furan conversion is lower in silylated catalysts. The increase activity in GaZSM (41%) comparing with ZSM (33%) may be due to Ga species. However, the lowest furan conversion observed on GaZSM* (24%) is again, due to the active sites that are killed by silica deposition. The significant decrease in overall xylene selectivity for the 2MF + propylene reactions is believed to be due to the furan itself not being a good Diels-Alder reaction agent for xylene production. The results for furan conversion using GaSD* are shown in Table 2. This table shows that the *para* selectivity for this catalyst is 87% and suggests that silylation may be used for an FCC catalyst to increase *p*-xylene yield from biomass conversion in a fluidized-bed reactor. This is shown below where GaSD* is used for pinewood conversion in a bubbled fluidized-bed reactor. Table 3 shows that an increase in *para* selectivity from 40% for GaSD to 72% for GaSD*.

Catalytic Conversion of Pinewood in a Fluidized-Bed Rreactor

CFP of pinewood is conducted in a fluidized bed reactor. The fluidized bed reactor has a two-inch (5.08 cm) diameter, a height of ten inches (25.4 cm), and is made of 316 stainless steel. Inside the reactor, the catalyst bed is supported by a distributor plate made of stacked 316 stainless mesh (300 mesh). Solid pinewood is introduced into the reactor from a sealed feed-hopper. Test runs are conducted using GaSD and GaSD*. Prior to the test runs, the pinewood is ground and sieved to a particle sized ranging between 0.25 – 1 mm. During the reaction, the catalyst is fluidized by helium gas flowing at 800 standard cubic centimeters (sccm) to enable the reactor to operate in the bubbling flow regime. The hopper and feed chamber are continuously purged with helium at 200 sccm to maintain an inert environment. The total gas flow through the reactor is 1000 sccm helium. Both the reactor and the inlet gas stream are heated to the reaction temperature (550°C). The reactor is given two hours to reach this temperature

before the reaction is started. The effluent gas leaving the reactor flows through a cyclone to remove entrained particles. The effluent then flows into 7 condensers in series to separate liquid and gas phase products. The first 3 condensers are placed in an ice-water bath with ethanol inside each condenser as a solvent, and the other 4 condensers are surrounded by a dry ice and acetone bath (–55°C), without any solvent inside the condensers. Uncondensed gas phase products are collected in air bags at 5, 10, 20, and 30 minutes after the biomass first enters the reactor. The reaction time is 30 minutes. After 30 minutes the reactor is purged using helium at a flow rate of 1000 sccm for 30 minutes to remove any CFP products other than coke on the catalyst. Liquid products are extracted from the condensers using ethanol. The catalyst is regenerated by using air at 800 sccm for 3 hours in addition to the 200 sccm helium from the feed chamber purge. During regeneration, the effluent gases pass through a copper converter where CO is converted to CO_2, and the CO_2 is trapped by a CO_2 trap. Gas phase products are analyzed by a GC-FID/TCD (Shimadzu 2014). Liquid samples are analyzed by a GC-FID (HP 7890). Coke yield is obtained by analyzing the weight change of the CO_2 trap. The results are shown in Table 3.

Table 3. Summary of pinewood conversions over GaSD and GaSD*.

Feed Stock	SWP	SWP	SWP
Catalyst	GaSD	GaSD*	GaSD*
T/°C	550	550	550
WHSV (space velocity)/h^{-1}	0.35	0.39	0.47
Overall Yield (carbon %)			
Aromatics	23.2	14.8	13.3
Olefins	8.9	6.3	5.9
Methane	1.5	3.8	3.3
CO_2	5.4	9.3	8.2
CO	17.2	22.9	19.6
Coke	33.3	33.4	30.0
Total	89.4	90.4	80.3
Aromatic Selectivity (%)			
Benzene	22.0	27.6	25.9
Toluene	29.4	35.8	35.3
Xylenes	18.5	15.5	16.3
Naphthalene	14.6	8.9	4.4
Ethylbenzene	2.6	2.3	1.7
Styrene	2.2	1.1	1.6
Phenol	1.0	1.0	1.7
Benzofuran	1.3	1.8	2.2
Indene	1.2	2.7	3.7
Methylnaphthalene	4.6	1.7	3.1
Xylene distribution (%)			
p-Xylene	40.0	70.7	72.4
m-Xylene	30.2	21.3	20.1
o-Xylene	29.8	7.97	7.50
Olefin Selectivity (%)			
Ethylene	46.0	44.4	44.9
Propylene	47.1	46.3	44.3
Butylene	4.31	4.30	4.96
Butadiene	2.54	5.00	5.79

While the invention has been explained in relation to various embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein includes any such modifications that may fall within the scope of the appended claims.

CLAIMS

1. A method for producing a fluid hydrocarbon product comprising p-xylene from a solid hydrocarbonaceous material, comprising:

feeding the solid hydrocarbonaceous material to a reactor;

pyrolyzing within the reactor at least a portion of the hydrocarbonaceous material under reaction conditions sufficient to produce a pyrolysis product; and

catalytically reacting at least a portion of the pyrolysis product under reaction conditions in the presence of a zeolite catalyst to produce the fluid hydrocarbon product;

the zeolite catalyst comprising pores with pore mouth openings and catalytic sites on the external surface of the catalyst, and an effective amount of a treatment layer derived from a silicone compound to reduce the size of the pore mouth openings and to render about 20% of the catalytic sites on the external surface of the catalyst inaccessible to the pyrolysis product.

2. The method of claim 1 wherein catalytic sites are positioned in the pores near the pore mouth openings, and the treatment layer renders at least about 20% of the catalytic sites in the pores near the pore mouth openings inaccessible to the pyrolysis product.

3. The method of claim 1 or claim 2 wherein the fluid hydrocarbon product comprises xylenes with a p-xylene selectivity in the xylenes of at least about 40%, or at least about 45%, or at least about 50%, or at least about 55%, or at least about 60%, or at least about 65%, or at least about 70%, or at least about 75%, or at least about 80%, or at least about 85%, or at least about 90%.

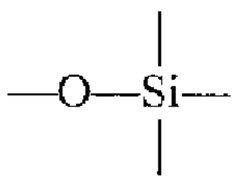
4. The method of any of the preceding claims wherein at least about 15%, or at least about 25%, or at least about 35%, or at least about 45%, or at least about 55%, or at least about 65%, or at least about 75%, or at least about 85%, or at least about 90%, or at least about 95%, or at least about 98%, or at least about 99%, of the catalytic sites on the external surface of the catalyst are inaccessible to the pyrolysis product.

5. The method of claim 2 wherein at least about 25%, or at least about 30% , or at least about 33%, or at least about 35%, or at least about 40%, or at least about 45%, or at least about 49%, or at least about 50%, or at least about 55%, or at least about 60%, or at least about 65%, or at least about 70%, or at least about 75%, or at least about 80%, or at least about 85%, or at least about 90%, or at least about 95% , or at least about 99% of the catalytic sites in the pores near the pore mouth openings are inaccessible to the pyrolysis product.

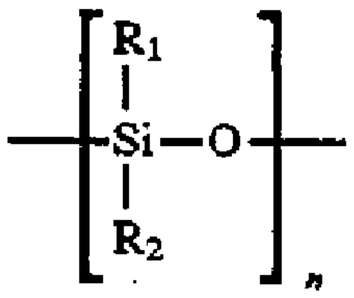
6. The method of any of the preceding claims, wherein the zeolite catalyst comprises silica and alumina, the silica to alumina molar ratio being in the range from about 10:1 to about 50:1, or in the range from about 10:1 to about 40:1, or in the range from about 10:1 to about 20:1, or about 15:1.

7. The method of claim 6, wherein the zeolite catalyst further comprises nickel, platinum, vanadium, palladium, manganese, cobalt, zinc, copper, chromium, gallium, an oxide of one or more thereof, or a mixture of two or more thereof.

8. The method of any of the preceding claims wherein the silicone compound comprises at least one group represented by the formula



9. The method of any of the preceding claims wherein the silicone compound is represented by the formula:



wherein R_1 and R_2 independently comprise hydrogen, halogen, hydroxyl, alkyl, alkoxyl, halogenated alkyl, aryl, halogenated aryl, aralkyl, halogenated aralkyl, alkaryl or halogenated alkaryl; and n is a number that is at least 2.

10. The method of claim 9 wherein R_1 and/or R_2 comprise methyl, ethyl, or phenyl.

11. The method of claim 9 or claim 10 wherein n is a number in the range from about 3 to about 1000.

12. The method of any of the preceding claims wherein the silicone compound has a number average molecular weight in the range from about 80 to about 20,000, or from about 150 to 10,000.

13. The method of any of the preceding claims wherein the silicone compound comprises dimethylsilicone, diethylsilicone, phenylmethylsilicone, methylhydrogensilicone, ethylhydrogen silicone, phenylhydrogen silicone, methylethyl silicone, phenylethyl silicone, diphenyl silicone, methyltrifluoropropyl silicone, ethyltrifluoropropyl silicone, polydimethyl silicone, tetrachloro-phenylmethyl silicone, tetrachlorophenylethyl silicone, tetrachlorophenylhydrogen silicone, tetrachlorophenylphenyl silicone, methylvinyl silicone, hexamethyl cyclotrisiloxane, octamethyl cyclotetrasiloxane, hexaphenyl cyclotrisiloxane, octaphenyl cyclotetrasiloxane, or a mixture of two or more thereof.

14. The method of any of claims 1 to 8 wherein the silicone compound comprises a tetraorthosilicate.

15. The method of claim 14 wherein the silicone compound comprises tetramethyl-orthosilicate, tetraethylorthosilicate, or a mixture thereof.

UMA 12-16 REPLACEMENT PAGE

16. The method of any of the preceding claims wherein the reactor comprises a continuously stirred tank reactor, a batch reactor, a semi-batch reactor, a fixed bed reactor or a fluidized bed reactor.

17. The method of any of claims 1 to 15 wherein the reactor comprises a fluidized bed reactor.

18. The method of any of the preceding claims, wherein the hydrocarbonaceous material comprises biomass.

19. The method of any of the preceding claims, wherein the hydrocarbonaceous material comprises plastic waste, recycled plastics, agricultural solid waste, municipal solid waste, food waste, animal waste, carbohydrates, lignocellulosic materials, xylitol, glucose, cellobiose, hemi-cellulose, lignin, sugar cane bagasse, glucose, wood, corn stover, or a mixture of two or more thereof.

20. The method of any of claims 1 to 17 wherein the hydrocarbonaceous material comprises pinewood.

21. The method of any of the preceding claims, wherein the reactor is at a temperature in the range from about 400°C to about 600°C, or from about 425 °C to about 500 °C, or from about 440 °C to about 460 °C.

22. The method of any of the preceding claims, wherein the hydrocarbonaceous material is fed to the reactor at a mass normalized space velocity of up to about 3 $hour^{-1}$, or up to about 2 $hour^{-1}$, or up to about 1.5 $hour^{-1}$, or up to about 0.9 $hour^{-1}$, or in the range from about 0.01 $hour^{-1}$ to about 3 $hour^{-1}$, or in the range from about 0.01 to about 2 $hour^{-1}$, or in the range from about 0.01 to about 1.5 $hour^{-1}$, or in the range from about 0.01 to about 0.9 $hour^{-1}$, or in the range from about 0.01 $hour^{-1}$ to about 0.5 $hour^{-1}$, or in the range from about 0.1 $hour^{-1}$ to about 0.9 $hour^{-1}$, or in the range from about 0.1 $hour^{-1}$ to about 0.5 $hour^{-1}$.

UMA 12-16

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23. The method of any of the preceding claims wherein the fluid hydrocarbon product comprises an aromatic compound, the aromatic carbon molar yield at least about 22%.

24. The method of any of claims 1 to 23 wherein the fluid hydrocarbon product comprises an olefinic compound, the olefin carbon molar yield being at least about 3%, or at least about 6%, or at least about 9%, or at least about 12 %.

25. The method of any of the preceding claims, further comprising the step of recovering the fluid hydrocarbon product.

26. The method of any of the preceding claims, wherein the fluid hydrocarbon product further comprises aromatic compounds and/or olefin compounds.

27. The method of any of the preceding claims, wherein the fluid hydrocarbon product further comprises benzene, toluene, ethylbenzene, methylethylbenzene, trimethylbenzene, o-xylene, m-xylene, indanes naphthalene, methylnaphthelene, dimethylnaphthalene, ethylnaphthalene, hydrindene, methylhydrindene, dimethylhydrindene, or a mixture of two or more thereof.

28. The method of any of the preceding claims wherein the mass yield of p-xylene in the fluid hydrocarbon product is at least about 1.5 wt%, or at least about 2 wt%, or at least about 2.5 wt%, or at least about 3 wt%.

29. The method of any of the preceding claims wherein the reactor is operated at a pressure of at least about 100 kPa, or at least about 200 kPa, or at least about 300 kPa, or at least about 400 kPa.

Duration: 20.03.2014 13:27:02 - 20.03.2014 13:35:34. This page 13 of 2014 13:34:44
Received at the EPO on Mar 20, 2014 13:35:34. Page 13 of 15

UMA 12-16

REPLACEMENT PAGE

30. The method of any of claims 1 to 28 wherein the reactor is operated at a pressure below about 600 kPa, or below about 400 kPa, or below about 200 kPa.

31. The method of any of claims 1 to 28 wherein the reactor is operated at a pressure in the range from about 100 to about 600 kPa, or in the range from about 100 to about 400 kPa, or in the range from about 100 to about 200 kPa.

32. The method of any of the preceding claims, wherein during the catalytically reacting step a dehydration, decarbonylation, decarboxylation, isomerization, oligomerization and/or dehydrogenation reaction is conducted.

33. The method of any of the preceding claims wherein the pyrolysis product is formed with less than about 30 wt%, or less than about 25 wt%, or less than about 20 wt%, or less than about 15 wt%, or less than about 10% of the pyrolysis product being coke.

34. The method of any of the preceding claims, wherein the pyrolyzing step and the catalytically reacting steps are carried out in a single vessel.

35. The method of any of claims 1 to 33, wherein the pyrolyzing step and the catalytically reacting steps are carried out in separate vessels.

36. The method of any of the preceding claims wherein the residence time for the hydrocarbonaceous material in the reactor is at least about 1 second, at least about 2 seconds, at least about 5 seconds, at least about 7 seconds, at least about 10 seconds, at least about 15 seconds, at least about 20 seconds, at least about 25 seconds, at least about 30 seconds, at least about 60 seconds, at least about 120 seconds, at least about 240 seconds, or at least about 480 seconds.

37. The method of any of the preceding claims wherein the contact time of the pyrolysis product with the catalyst is at least about 1 second, at least about 2 seconds, at least about 5 seconds, at least about 7 seconds, at least about 10 seconds, at least about 15 seconds, at least about 20 seconds, at least about 25 seconds, at least about 30 seconds, at least about

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Received at the EPO on Mar 20, 2014 13:35:34. Page 14 of 15

UMA 12-16

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60 seconds, at least about 120 seconds, at least about 240 seconds, or at least about 480 seconds.

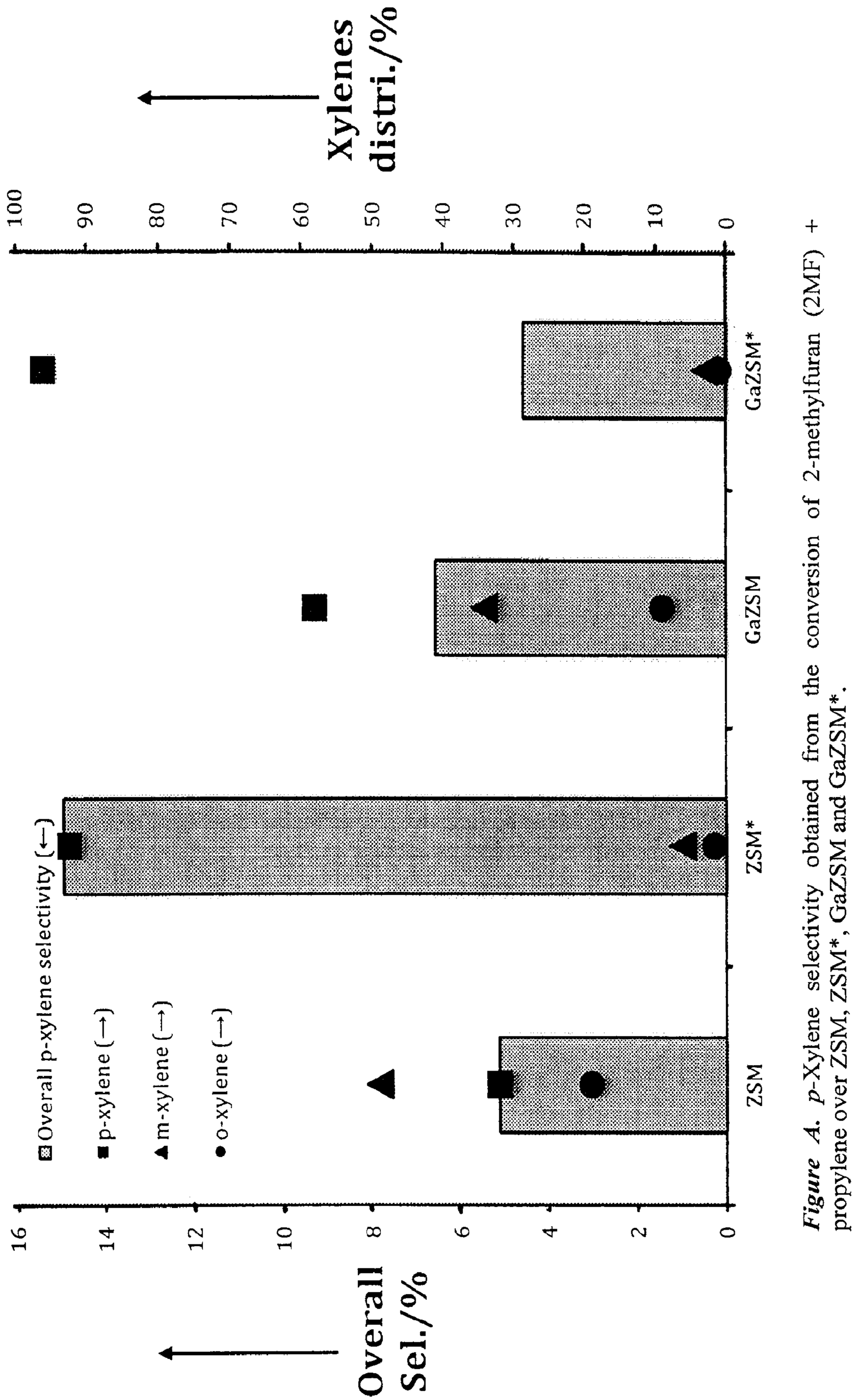


Figure A. *p*-Xylene selectivity obtained from the conversion of 2-methylfuran (2MF) + propylene over ZSM, ZSM*, GaZSM and GaZSM*.

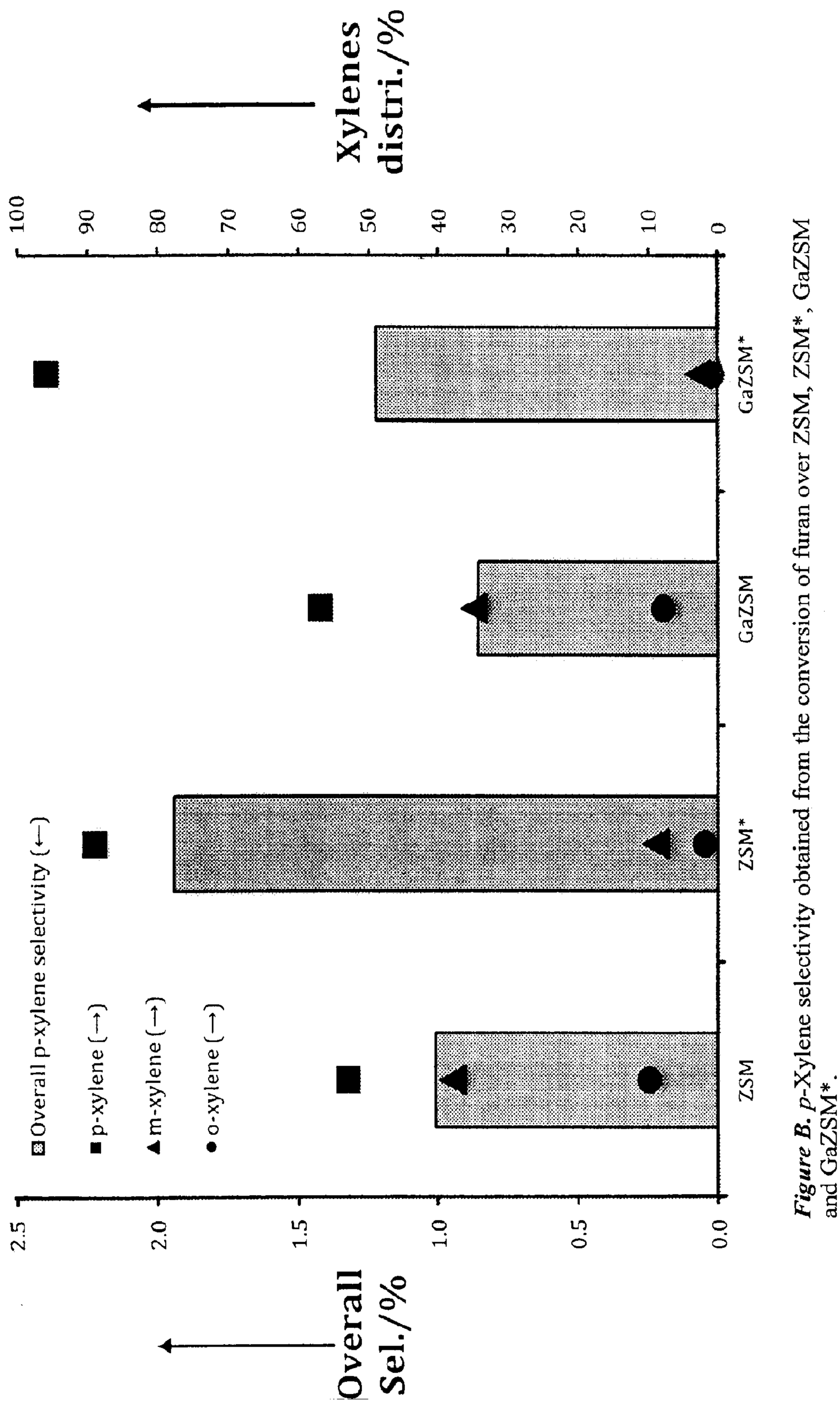


Figure B. *p*-Xylene selectivity obtained from the conversion of furan over ZSM, ZSM*, GaZSM and GaZSM*.

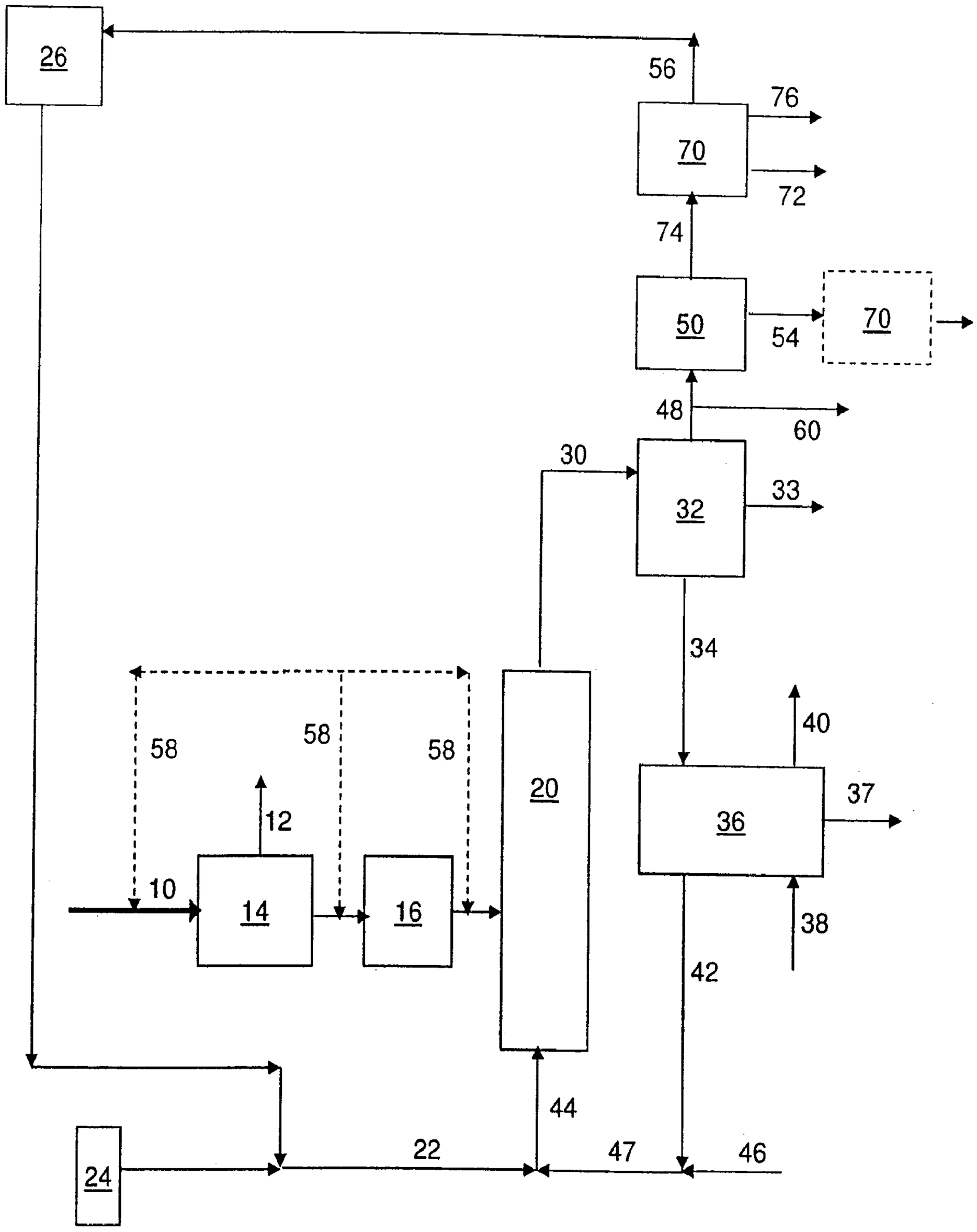

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FIG. 1A

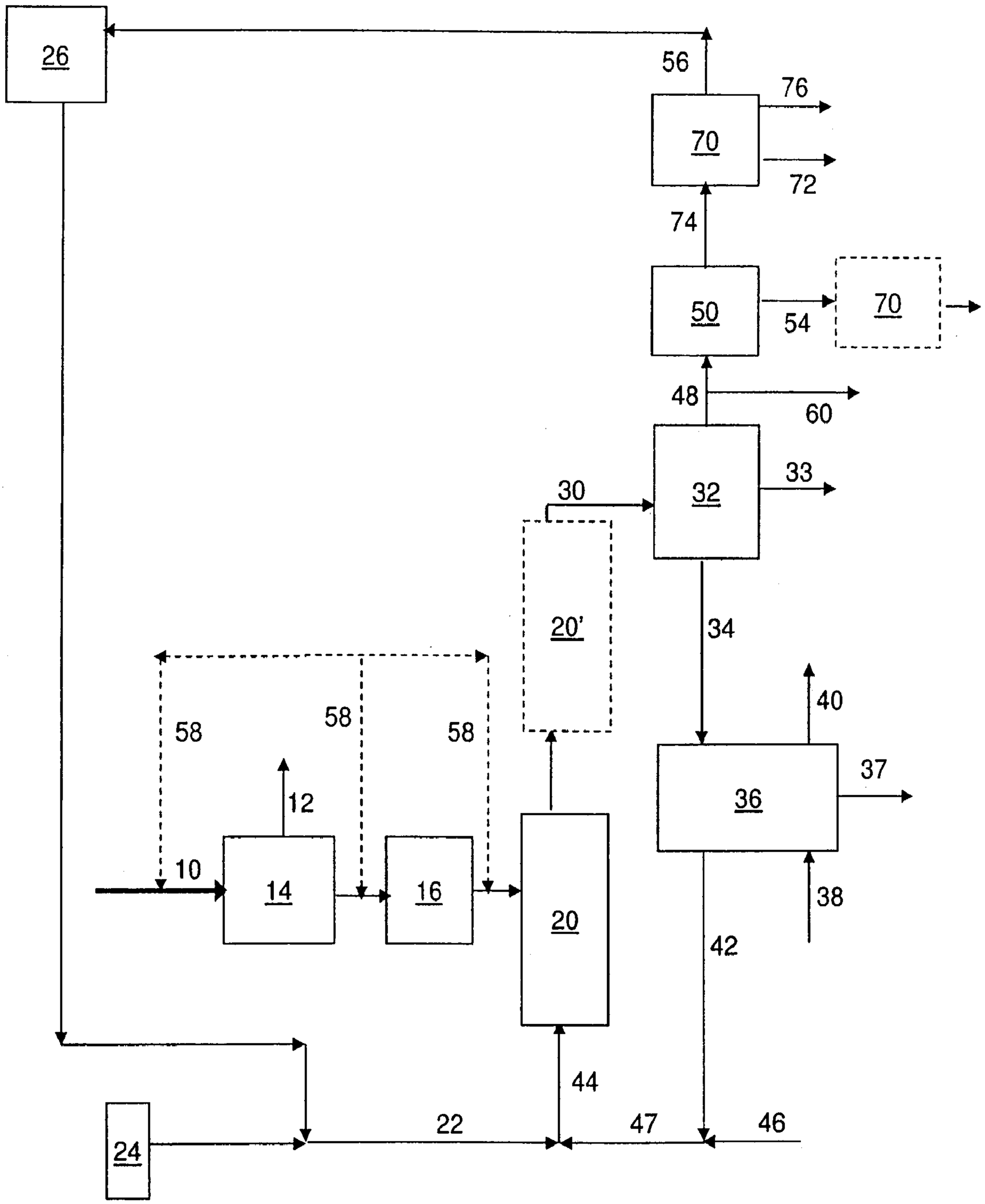

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FIG. 1B

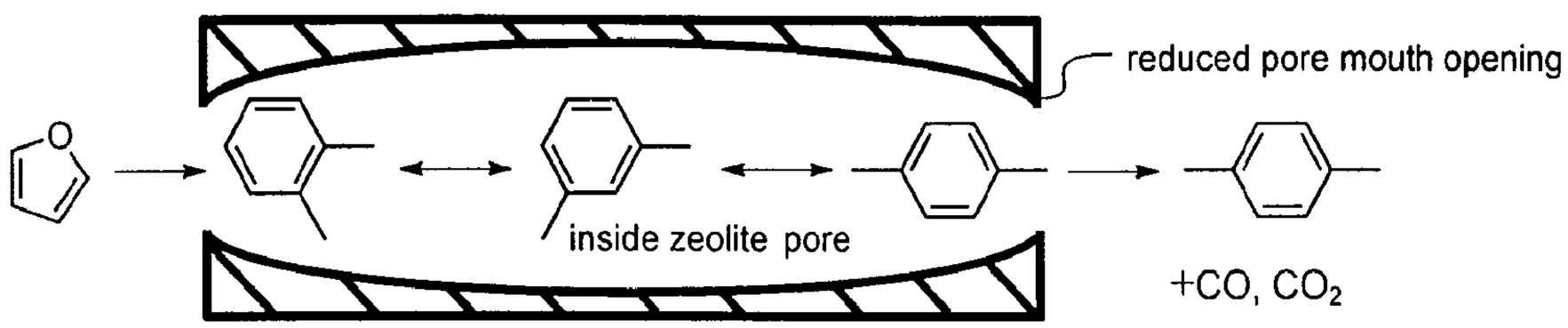


FIG. 2