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Sorensen(10) **Pub. No.: US 2016/0145496 A1**(43) **Pub. Date: May 26, 2016**(54) **CATALYTIC FAST PYROLYSIS PROCESS**(71) Applicant: **Anellotech, Inc.**, Pearl River, NY (US)(72) Inventor: **Charles Sorensen**, Haverstraw, NY (US)(21) Appl. No.: **14/920,488**(22) Filed: **Oct. 22, 2015****Related U.S. Application Data**

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(2013.01); **C10B 27/06** (2013.01)(57) **ABSTRACT**

The present invention provides an improved catalytic fast pyrolysis process for increased yield of useful and desirable products. The process comprises the steps of: a) feeding biomass, a specific catalyst composition and transport fluid to a catalytic fast pyrolysis process fluidized bed reactor maintained at reaction conditions to manufacture a raw fluid product stream, b) feeding the raw fluid product stream of step a) to a catalyst separation and stripping system to produce separated catalyst and a fluid product stream, c) feeding the fluid product stream of step b) to a vapor/liquid separation system to produce a liquid phase stream and a vapor phase stream comprising benzene, toluene and xylenes, d) feeding the vapor phase stream of step c) to a product recovery system to recover benzene, toluene and xylenes, and e) recycling at least a portion of the recovered toluene of step d) to the fluidized bed reactor of step a).

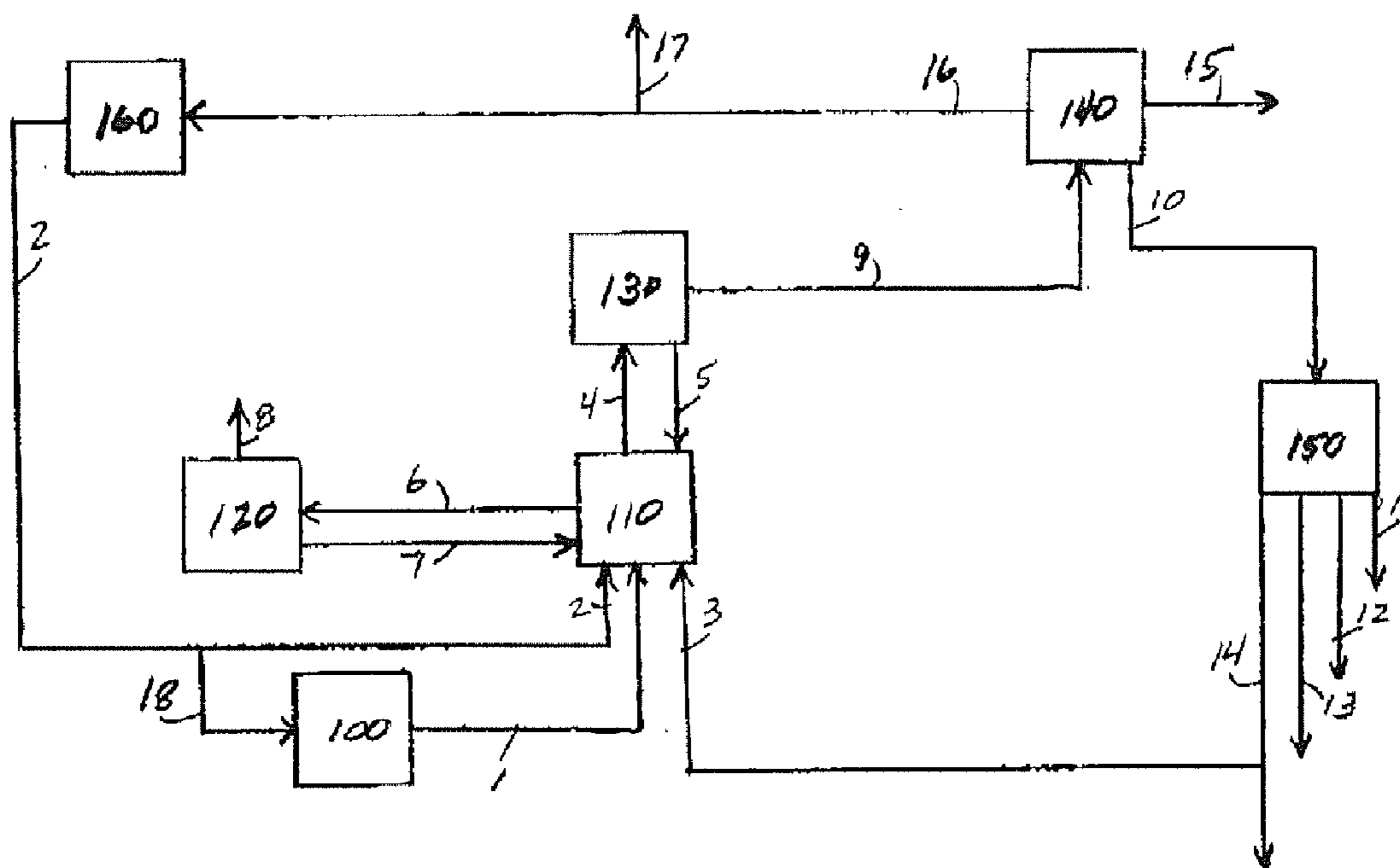
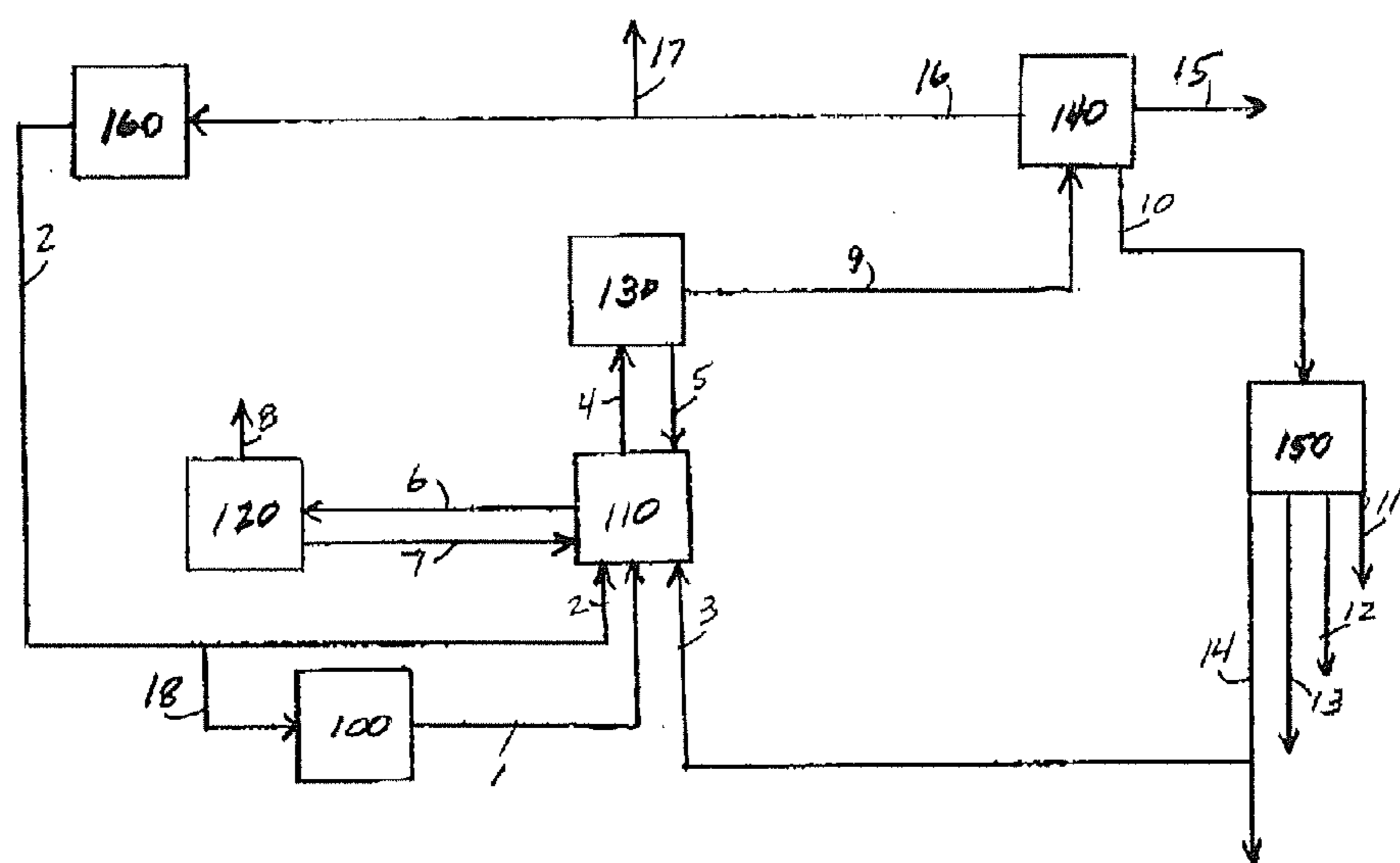


Figure 1



CATALYTIC FAST PYROLYSIS PROCESS**FIELD OF THE INVENTION**

[0001] The present invention relates to an improved catalytic fast pyrolysis process. In particular, it relates to an improved catalytic fast pyrolysis process for producing benzene and xylenes.

BACKGROUND OF THE INVENTION

[0002] The needs for travel and consumer goods have driven the ever increasing consumption of fossil fuels such as coal and oil, typically obtained from deep underground. The extraction of fossil fuels by mining and drilling has often been accompanied by environmental and political costs. Furthermore, as the more accessible sources of fossil fuels are being used up, this has led to the pursuit of more expensive extraction technologies such as fracking and deep sea drilling. Additionally, the consumption of fossil fuels causes higher levels of atmospheric carbon, typically in the form of carbon dioxide.

[0003] To reduce these problems, there have been extensive efforts made in converting biomass to fuels and other useful chemicals. Unlike fossil fuels, biomass is renewable and carbon-neutral; that is, biomass-derived fuels and chemicals do not lead to increased atmospheric carbon since the growth of biomass consumes atmospheric carbon.

[0004] Much of the work on biomass has involved converting refined biomass including vegetable oils, starches, and sugars; however, since these types of refined biomass may alternatively be consumed as food, there is even a greater utility for converting non-food biomass such as agricultural waste (bagasse, straw, corn stover, corn husks, etc.), energy crops (like switch grass and saw grass), trees and forestry waste, such as wood chips and saw dust, waste from paper mills, plastic waste, recycled plastics or algae, in combination sometimes referred to as cellulosic biomass. Biomass generally includes three main components: lignin, hemicellulose, and cellulose.

[0005] Generating fuels and chemicals from biomass requires specialized conversion processes different from conventional petroleum-based conversion processes due to the nature of the feedstock. High temperatures, solid feed, high concentrations of water, unusual separations, and oxygenated by-products are some of the features of biomass conversion that are distinct from those encountered in petroleum upgrading. Thus, despite extensive efforts, there are many challenges that must be overcome to efficiently produce chemicals or fuels from biomass.

[0006] A variety of biomass-derived polymeric materials such as lignin, cellulose, and hemicellulose, can be pyrolyzed to produce mixtures of aromatics, olefins, carbon monoxide (CO), carbon dioxide (CO₂), water, and other products. A particularly desirable form of pyrolysis is known as catalytic fast pyrolysis (CFP) which involves the conversion of biomass in a catalytic fluid bed reactor to produce a mixture of aromatics, olefins, and a variety of other materials. The aromatics include benzene, toluene, xylenes (collectively BTX), and naphthalene, among other aromatics. The olefins include ethylene, propylene, and lesser amounts of higher molecular weight olefins.

[0007] The raw effluent from a CFP process is a complex mixture that comprises aromatics, olefins, oxygenates, paraffins, H₂, CH₄, CO, CO₂, water, char, ash, coke, catalyst fines,

and a host of other compounds. Manufacture, separation and recovery of the various components, especially those found to be more valuable, from this complex mixture is increasingly important.

[0008] In U.S. Patent Publication No. 2014/0107306 A1, a method and apparatus are described for pyrolysis of biomass and conversion of at least one pyrolysis product to another chemical compound. The latter method comprises feeding a hydrocarbonaceous material to a reactor, pyrolyzing within the reactor at least a portion of the hydrocarbonaceous material under reaction conditions sufficient to produce one or more pyrolysis products, catalytically reacting at least a portion of the pyrolysis products, separating at least a portion of the hydrocarbon products, and reacting a portion of the hydrocarbon products to produce a chemical intermediate.

[0009] In U.S. Pat. No. 8,277,643; U.S. Pat. No. 8,864,984; U.S. Patent Publication No. 2012/0203042 A1; U. S. Patent Publication No. 2013/0060070 A1, U. S. Patent Publication No. 2014/0027265 A1; and US Patent Publication No. 2014/0303414 A1, each incorporated herein by reference in its entirety, apparatus and process conditions suitable for CFP are described.

[0010] It is a general goal of the technology to provide high yields of BTX as these are usually the most valuable products. Under operating conditions currently employed in CFP, more toluene than either benzene or mixed-xylene products is made. However the value of toluene can be less than either benzene or xylene, so it is desirable to increase production of benzene and xylenes from conversion of biomass in pyrolysis or CFP.

[0011] In conventional aromatics processing, the toluene can be converted to an equilibrium mixture of benzene and xylenes by disproportionation in a fixed bed reactor operating at elevated pressure and in the presence of added hydrogen gas. Such a disproportionation process is disclosed in U.S. Pat. Nos. 4,052,476; 4,851,604; and 6,958,305; illustrative of a group of disclosures of such a mechanism. These processes do not convert biomass in a CFP fluidized bed to produce enhanced amounts of benzene and xylenes. Further, U.S. Pat. No. 7,563,358 is illustrative of a group of other disclosures of a mechanism for producing an aromatic product of benzene, toluene, xylenes from a hydrocarbon feed comprising: (a) C₆⁺ non-aromatic cyclic hydrocarbons; (b) C₈⁺ single-ring aromatic hydrocarbons having at least one alkyl group containing two or more carbon atoms; and (c) C₉⁺ single-ring aromatic hydrocarbons having at least three methyl groups.

[0012] In light of current commercial practices and the disclosures of art, a simple economical process for enhancing production of benzene and xylenes from a catalytic pyrolysis process is needed. The present invention provides such a process.

SUMMARY OF THE INVENTION

[0013] Various aspects of the present invention include increased yield of useful and desirable benzene and xylene products in a CFP process. The present invention provides for this in an economical improved process. An embodiment of the present process comprises the steps of: a) feeding biomass, catalyst composition, such as one comprising a crystalline molecular sieve characterized by a silica/alumina mole ratio (SAR) greater than 12 and a Constraint Index from 1 to 12, and transport fluid to a CFP process fluidized bed reactor maintained at reaction conditions to manufacture a raw fluid product stream, b) feeding the raw fluid product stream of

step a) to a solids separation and stripping system to produce separated solids and a fluid product stream, c) feeding the fluid product stream of step b) to a vapor/liquid separation system to produce a liquid phase stream comprising components selected from the group consisting of water, char, coke, ash, catalyst fines and combinations thereof, and a vapor phase stream comprising benzene, toluene and xylenes, d) feeding the vapor phase stream of step c) to a product recovery system to recover benzene, toluene and xylenes, and e) recycling at least a portion of the recovered toluene of step d) to the fluidized bed reactor of step a).

[0014] Another embodiment of the present invention comprises such process wherein the crystalline molecular sieve of the catalyst of step a) has a structure of ZSM-5, ZSM-1, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-38, ZSM-48, ZSM-50 or combinations thereof.

[0015] Another embodiment of the invention process comprises such process wherein the crystalline molecular sieve of the catalyst of step a) is characterized by an SAR from greater than 12 to 240 and a Constraint Index from 5 to 10, such as a crystalline molecular sieve selected from those having the structure of ZSM-5, ZSM-11, ZSM-22, ZSM-23 or combinations thereof.

[0016] Another embodiment of the invention process comprises the steps of: a) feeding biomass, catalyst composition comprising a crystalline molecular sieve having the structure of ZSM-5, and transport fluid to a CFP process fluidized bed reactor maintained at reaction conditions including a temperature from 300 to 1000° C. and pressure from 100 to 1500 kPa to manufacture a raw fluid product stream, b) feeding the raw fluid product stream of step a) to a catalyst separation and stripping system to produce separated catalyst and a fluid product stream, c) feeding the fluid product stream of step b) to a vapor/liquid separation system to produce a liquid phase stream comprising components selected from the group consisting of water, char, coke, ash, catalyst fines and combinations thereof, and a vapor phase stream comprising benzene, toluene and xylenes, d) feeding the vapor phase stream of step c) to a product recovery system to recover benzene, toluene and xylenes, and e) recycling from about 5 to about 99% of the recovered toluene of step d) to the fluidized bed reactor of step a).

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] FIG. 1 is a block flow illustration of an embodiment of the present process.

DETAILED DESCRIPTION OF THE INVENTION

[0018] As a result of extensive research in view of the above, we have found that we can economically and effectively conduct a CFP process to enhance manufacture of valuable benzene and xylenes product by way of a series of sequential steps.

[0019] The present improved process comprises steps of: a) feeding biomass, such as, for example, that provided from renewable sources of organic materials, catalyst composition comprising one or more of a particular family of crystalline molecular sieves, for example, those characterized by a SAR greater than 12 and a Constraint Index from 1 to 12, and transport fluid to a CFP process fluidized bed reactor maintained at specific reactions conditions, for example, a temperature from 300 to 1000° C. and pressure from 100 to 1500 kPa, to manufacture a raw fluid product stream, b) feeding the

raw fluid product stream of step a) to a solids separation and stripping system, hereinafter more particularly described, to produce separated solids and a fluid product stream, c) feeding the fluid product stream of step b) to a vapor/liquid separation system, hereinafter more particularly described, to produce a liquid phase stream comprising various components, such as those selected from the group consisting of water, char, coke, ash, catalyst fines and combinations thereof, and a vapor phase stream comprising benzene, toluene, xylenes and other aromatic compounds, d) feeding the vapor phase stream of step c) to a product recovery system, hereinafter more particularly described, to recover benzene, toluene and xylenes, and e) recycling at least a portion of the recovered toluene of step d) to the fluidized bed reactor of step a).

[0020] As used herein, 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 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-ethyltoluene, 3-ethyltoluene, 4-ethyltoluene, trimethylbenzene (e.g., 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, etc.), ethylbenzene, styrene, cumene, n-propylbenzene, xylenes (e.g., p-xylene, m-xylene, o-xylene), naphthalene, methylnaphthalene (e.g., 1-methylnaphthalene), anthracene, 9,10-dimethylantracene, pyrene, phenanthrene, dimethyl naphthalene (e.g., 1,5-dimethylnaphthalene, 1,6-dimethylnaphthalene, 2,5-dimethylnaphthalene, etc.), ethyl naphthalene, hydrindene, methylhydrindene, and dimethylhydrindene. Single ring and/or higher ring aromatics may also be produced in some embodiments. Aromatics also include single and multiple ring compounds that contain heteroatom substituents, i.e., phenol, cresol, benzofuran, aniline, indole, etc.

[0021] As used herein, the term “biomass” has its conventional meaning in the art and refers to any organic source of energy or chemicals that is renewable. Its major components can be: (1) trees (wood) and all other vegetation; (2) agricultural products and wastes (corn, fruit, garbage ensilage, etc.); (3) algae and other marine plants; (4) metabolic wastes (manure, sewage), and (5) cellulosic urban waste. Examples of biomass materials are described, for example, in Huber, G. W. et al, “Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering,” Chem. Rev. 106, (2006), pp. 4044-4098.

[0022] Biomass is conventionally defined as the living or recently dead biological material that can be converted for use as fuel or for industrial production. The criterion as biomass is that the material should be recently participating in the carbon cycle so that the release of carbon in the combustion process results in no net increase averaged over a reasonably short period of time (for this reason, fossil fuels such as peat, lignite and coal are not considered biomass by this definition as they contain carbon that has not participated in the carbon cycle for a long time so that their combustion results in a net increase in atmospheric carbon dioxide). Most commonly, biomass refers to plant matter grown for use as biofuel, but it also includes plant or animal matter used for production of fibers, chemicals or heat. Biomass may also include biodegradable wastes or byproducts that can be burned as fuel or converted to chemicals, including municipal wastes, green waste (the biodegradable waste comprised of garden or park waste, such as grass or flower cuttings and hedge trimmings),

byproducts of farming including animal manures, food processing wastes, sewage sludge, and black liquor from wood pulp or algae. Biomass excludes organic material which has been transformed by geological processes into substances such as coal, oil shale or petroleum. Biomass is widely and typically grown from plants, including miscanthus, spurge, sunflower, switchgrass, hemp, corn (maize), poplar, willow, sugarcane, and oil palm (palm oil) with the roots, stems, leaves, seed husks and fruits all being potentially useful. Processing of the raw material for introduction to the processing unit may vary according to the needs of the unit and the form of the biomass.

[0023] As used herein, the terms “olefin” or “olefin compound” (a.k.a. “alkenes”) have their ordinary meaning in the art, and refer to any unsaturated hydrocarbon containing one or more pairs of carbon atoms linked by a double bond. Olefins 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 include, but are not limited to, ethene, propene, allene (propadiene), 1-butene, 2-butene, isobutene (2-methylpropene), butadiene, and isoprene, among others. Examples of cyclic olefins include cyclopentene, cyclohexene, and 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.

[0024] As used herein, the term “oxygenate” includes any organic compound that contains at least one atom of oxygen in its structure such as alcohols (e.g., methanol, ethanol, etc.), acids (e.g., acetic acid, propionic acid, etc.), aldehydes (e.g., formaldehyde, acetaldehyde, etc), esters (e.g., methyl acetate, ethyl acetate, etc.), ethers (e.g., dimethyl ether, diethyl ether, etc.), aromatics with oxygen containing substituents (e.g., phenol, cresol, benzoic acid etc.), cyclic ethers, acids, aldehydes, and esters (e.g. furan, furfural, etc.), and the like.

[0025] As used herein, the terms “pyrolysis” and “pyrolyzing” have their conventional meaning in the art and refer to the transformation of a compound, e.g., a solid hydrocarbonaceous material, into one or more other substances, e.g., volatile organic compounds, gases and coke, by heat, preferably without the addition of, or in the absence of, oxygen. Preferably, the volume fraction of oxygen present in a pyrolysis reaction chamber is 0.5% or less. Pyrolysis may take place with or without the use of a catalyst. “Catalytic pyrolysis” refers to pyrolysis performed in the presence of a catalyst, and may involve steps as described in more detail below. Catalytic fast pyrolysis (CFP) that involves the conversion of biomass in a catalytic fluid bed reactor to produce a mixture of aromatics, olefins, and a variety of other materials is a particularly beneficial pyrolysis process. Examples of catalytic pyrolysis processes are outlined, for example, in Huber, G. W. et al, “Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering,” Chem. Rev. 106, (2006), pp. 4044-4098, incorporated herein by reference.

[0026] As used herein, the term “recovery” of a component is the fraction (or percent) of that component that is present in the recovered product stream(s) compared to the amount of that component that is present in the reactor effluent stream. For example if 10 grams of “A” is present in the reactor

effluent and 8.5 grams of “A” is present in the recovered product stream, then the recovery of “A” is 8.5/10 or 0.85 (85%). All percentages provided herein are by mass unless otherwise indicated.

[0027] The catalyst composition required in the CFP process fluidized bed reactor of the present invention comprises a crystalline molecular sieve characterized by an SAR greater than 12 and a Constraint Index from 1 to 12. Non-limiting examples of these crystalline molecular sieves are those having the structure of ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-50 or combinations thereof. As an embodiment, the catalyst composition comprises a crystalline molecular sieve characterized by an SAR from greater than 12 to 240 and a Constraint Index from 5 to 10, such as, for example, molecular sieves having the structure of ZSM-5, ZSM-11, ZSM-22, ZSM-23 or combinations thereof.

[0028] The members of the class of molecular sieves useful herein have an effective pore size of generally from about 5 to about 8 Angstroms, such as to freely sorb normal hexane. In addition, the molecular sieve structure must provide constrained access to larger molecules. For example, if the only pore windows in a molecular sieve structure are formed by 8-membered rings of silicon and aluminum atoms, then access by molecules of larger cross-section than normal hexane is excluded and the molecular sieve is not of the desired type for use herein. Windows of 10-membered rings are preferred, although, in some instances, excessive puckering of the rings or pore blockage may render these molecular sieves ineffective.

[0029] A convenient measure of the extent to which a molecular sieve provides control to molecules of varying sizes to its internal structure is the Constraint Index of the crystal. Crystalline materials which provide a highly restricted access to and egress from its internal structure have a high value for the Constraint Index, and materials of this kind usually have pores of small size, e.g. less than 5 Angstroms. On the other hand, crystalline materials which provide relatively free access to the internal crystal structure have a low value for the Constraint Index, and usually have pores of large size, e.g. greater than 8 Angstroms. A simple determination of the Constraint Index may be made by passing continuously a mixture of an equal weight of normal hexane and 3-methylpentane over a small sample, approximately 1 gram or less, of crystalline material at atmospheric pressure according to the following procedure. The sample of the crystalline material, in the form of pellets or extrudate, is crushed to a particle size about that of coarse sand and mounted in a glass tube. Prior to testing, the crystalline material is treated with a stream of air at 537° C. for at least 15 minutes. The crystalline material is then flushed with helium and the temperature adjusted between 287° C. and 510° C. or higher to allow an overall conversion of between 10 and 60% when the mixture of hydrocarbons is passed at 1 liquid hourly space velocity (i.e., 1 volume of liquid hydrocarbon per volume of crystalline material per hour) over the crystalline material with a helium dilution to give a helium to total hydrocarbon mole ratio of 4:1. After 20 minutes on stream, a sample of the effluent is analyzed, most conveniently by gas chromatography, to determine the fraction remaining unchanged for each of the two hydrocarbons. The Constraint Index is the ratio of the log of the n-hexane remaining divided by the log of the 3-methylpentane remaining. The Constraint Index approximates the ratio of the cracking rate constants for the two

hydrocarbons. The method by which Constraint Index is determined is described more fully in U.S. Pat. No. 4,029, 716, incorporated by reference for details of the method.

[0030] Constraint Index (CI) values for some typical materials are:

	CI	Test Temp, ° C.
ZSM-4	0.5	316
ZSM-5	6-8.3	371-316
ZSM-11	5-8.7	371-316
ZSM-12	2.3	316
ZSM-20	0.5	371
ZSM-22	7.3	427
ZSM-23	9.1	427
ZSM-34	50	371
ZSM-35	4.5	454
ZSM-48	3.5	538
ZSM-50	2.1	427
Mordenite	0.5	316
REY	0.4	316
Dealuminized Y	0.5	510
Beta	0.6-2	316-399

[0031] CI values typically characterize the specified crystalline material, but are the cumulative result of several variables useful in the determination and calculation thereof. Thus, for a given crystal exhibiting a CI value within the range of 1 to 12, depending on the temperature employed during the test method, with accompanying conversion between 10 and 60%, the CI may vary within the indicated range of 1 to 12. Likewise, other variables such as crystal size or the presence of possibly occluded contaminants and binders intimately combined with the crystal may affect the CI. It is understood to those skilled in the art that the CI, as utilized herein, while affording a highly useful means for characterizing the molecular sieves of interest is approximate, taking into consideration the manner of its determination, with the possibility, in some instances, of compounding variable extremes. However, in all instances, at a temperature within the above-specified range, the CI will have a value for any given molecular sieve useful herein within the approximate range of 1 to 12.

[0032] The molecular sieve for use herein or the catalyst composition comprising same may be thermally treated at high temperatures. This thermal treatment is generally performed by heating at a temperature of at least 370° C. for a least 1 minute and generally not longer than 20 hours (typically in an oxygen containing atmosphere, preferably air). While subatmospheric pressure can be employed for the thermal treatment, atmospheric pressure is desired for reasons of convenience. The thermal treatment can be performed at a temperature up to 925° C. The thermally treated product is particularly useful in the present process.

[0033] For the catalyst composition useful in this invention, the suitable molecular sieve may be employed in combination with a support or binder material such as, for example, a porous inorganic oxide support or a clay binder. Non-limiting examples of such binder materials include alumina, zirconia, silica, magnesia, thoria, titania, boria and combinations thereof, generally in the form of dried inorganic oxide gels and gelatinous precipitates. Suitable clay materials include, by way of example, bentonite, kieselguhr and combinations thereof. The relative proportion of suitable crystalline molecular sieve of the total catalyst composition may vary widely with the molecular sieve content ranging from 30 to 90

percent by weight and more usually in the range of 40 to 70 percent by weight of the composition. The catalyst composition may be in the form of an extrudate, beads or fluidizable microspheres.

[0034] The molecular sieve for use herein or the catalyst composition comprising it may have original cations replaced, in accordance with techniques well known in the art, at least in part, by ion exchange with hydrogen or hydrogen precursor cations and/or non-noble metal ions of Group VIII of the Periodic Table, i.e. nickel, iron and/or cobalt.

[0035] Examples of apparatus and process conditions suitable for the CFP process are described in U.S. Pat. Nos. 8,277,643 and 8,864,984, and U. S. Patent Publication Nos. 2012/0203042 A1, 2014/0027265 A1, 2014/0303414 A1 and 2013/0060070A1, each incorporated herein by reference. Conditions for CFP of biomass may include one or a combination of the following features (which are not intended to limit the broader aspects of the invention): a catalyst composition; that catalyst composition comprising a metal selected from the group consisting of titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium, platinum, palladium, silver, phosphorus, sodium, potassium, magnesium, calcium, tungsten, zirconium, cerium, lanthanum, and combinations thereof; a fluidized bed, circulating bed, moving bed, or riser reactor; an operating temperature in the range of 300 to 1000° C.; and a solid catalyst/biomass mass ratio of from 0.1 to 40.

[0036] Referring more particularly to FIG. 1, which shows a block flow illustration of an embodiment of the present process. Biomass feedstock is prepared by chipping, drying, grinding, washing or other processes, or some combination of these in biomass preparation system **100**, and fed to CFP fluid bed reactor **110** via line **1**. Catalyst composition comprising a crystalline molecular sieve characterized by an SAR greater than 12 and a CI from 1 to 12, e.g. having the structure of ZSM-5, and transport fluid, e.g. recycle gas, are introduced to the CFP reactor **110** via lines **7** and **2**, respectively. The CFP reactor is fluidized by the recycle gas or other fluid. The raw fluid product stream from the CFP reactor **110** is provided to solids separation and stripping system **130** via line **4**. Spent solid material from reactor **110** is passed to a catalyst regeneration system **120** via line **6** where it is regenerated by removing coke and char and generating steam, and the regenerated catalyst is returned to reactor **110** via line **7**. Excess steam from the catalyst regeneration system **120** may be sent to other processes or uses via line **8**. A portion of the separated solids from solids separation and stripping system **130** may be passed back to reactor **110** via line **5**, and fluid product from system **130** is passed to quench and vapor/liquid separation system **140** via line **9**. In vapor/liquid separation system **140** are produced a liquid phase stream comprising components selected from the group consisting of water, char, coke, ash, catalyst fines and combinations thereof, and a vapor phase stream comprising benzene, toluene, xylenes and other aromatics. Water is removed from vapor/liquid separation system **140** via line **15**, vapor phase stream comprising benzene, toluene and xylenes is removed via line **10**, and the remainder of components is removed via line **16**. A portion of the line **16** components may be passed to recycle compressor **160**, and then to CFP reactor **110** via line **2** as recycle gas for fluidization purposes. A portion, such as, for example, from 5 to 25%, of the compressed recycle gas in line **2** may be passed via line **18** to biomass preparation system **100**. From line **16** a portion of the stream may be taken as a purge of, for

example, from 5 to 50%, via line **17** in order to prevent the buildup of inert materials in the system. The stream of line **10** is passed to product recovery system **150** for recovery of benzene, toluene, xylenes and other aromatics. From product recovery system **150** is obtained benzene via line **11**, xylenes via line **12**, toluene via line **14**, and other aromatics via line **13**. At least a portion, such as from 5 to 99%, for example from 10 to 95%, such as from 30 to 50%, of the contents of line **14** is passed to CFP reactor **110** via line **3** as recycle. Recycle stream **3** can be fed to reactor **110** as a separate stream, or it can be combined with the fluidization fluid stream **2** (not shown), or it can be combined with the biomass stream **1** (not shown), or it can be combined with stream **7** (not shown), or it can be combined with a fresh catalyst stream (not shown), or any combination of these.

[0037] The CFP reactor **110** may be operated at a temperature from 300 to 1000° C., and the raw fluid product stream from reactor **110** is typically at a temperature of 300 to 620° C., such as 400 to 575° C., for example 500 to 550° C., and a pressure of 100 kPa to 1500 kPa, such as 200 kPa to 1000 kPa, for example 300 kPa to 700 kPa (pressures expressed as absolute pressures). The raw fluid product stream from reactor **110** comprises aromatics, olefins, oxygenates, paraffins, H₂, CH₄, CO, CO₂, water, char, ash, coke, catalyst fines, and a host of other components. On a water-free and solids-free basis the raw fluid product stream can comprise 20 to 60%, such as 25 to 55%, for example 30 to 50% CO; 10 to 50%, such as 15 to 40%, for example 20 to 35% CO₂; 0.1 to 10%, such as 0.2 to 5%, for example 0.3 to 1.0% H₂; 2 to 15%, such as 3 to 10%, for example 4 to 8% CH₄; 2 to 40%, such as 3 to 35%, for example 4 to 30%, BTX; 0.1 to 10%, such as 0.2 to 5%, for example 0.3 to 3% oxygenates; and 1 to 15%, such as 2 to 10%, for example 3 to 6% C₂-C₄ olefins. On a water-free and solids-free basis the raw fluid product stream can comprise a vapor mixture where the sum of CO and CO₂ is 30 to 90%, such as 40 to 85%, for example 50 to 80%.

[0038] Quenching with, for example, water in the vapor/liquid separation system **140** may be conducted at conditions of temperature from -5 to 200° C., such as from 10 to 100° C., for example from 40 to 80° C., and pressure of 150 to 1500 kPa, for example from 300 to 700 kPa. The product resulting from such a quenching step may then be compressed at conditions of 100 to 8000 kPa, for example 600 to 2000 kPa, and then cooled at conditions of -30 to 60° C., for example 5 to 30° C.

[0039] The solids separation and stripping system (e.g. **130** of FIG. 1) of step b) of the present process may include unit operations known to effectively separate entrained catalyst and certain other components from the raw fluid product stream of the CFP process. That raw fluid product stream may comprise entrained catalyst, catalyst fines, char, coke, ash, water, C₉⁺ aromatics, oxygenates, benzene, toluene, xylenes, CO, CO₂, CH₄, N₂, H₂, C₂-C₄ olefins and paraffins, and other compounds. Embodiments of such unit operations include one or more cyclones (such as, for example, in series), screens, filters, or some combination of these.

[0040] The vapor/liquid separation system (e.g. **140** of FIG. 1) of step c) of the present process may include unit operations known to effectively accomplish separation of the fluid product stream of step b) into a liquid phase stream comprising components selected from the group consisting of water, char, coke, ash, catalyst fines and combinations thereof, and a vapor phase stream comprising benzene, toluene and xylenes. Embodiments of such unit operations include venturi, quench

systems, condensers, chillers, absorption systems, scrubbers, demisters, or combinations of these.

[0041] The product recovery system (e.g. **150** of FIG. 1) of step d) of the present process may include unit operations known to effectively accomplish separation and recovery of benzene, toluene, xylenes and other aromatic compounds from the vapor phase of step c). Embodiments of such unit operations include condensers, chillers, absorption systems, demisters, or combinations of these.

[0042] The following Example demonstrates the present invention and its capability for use. The invention is capable of other and different embodiments, and its several details are capable of modifications in various apparent respects, without departing from the spirit and scope of the invention. Accordingly, the Example is to be regarded as illustrative in nature and not as restrictive. All percentages are by mass unless otherwise indicated.

Example

[0043] A calculation approach was used to develop a conservative estimate of toluene conversion in a CFP process fluidized bed with the understanding that the CFP BTX product may not be at equilibrium. A representative BTX composition of a CFP process was mathematically converted to the chemical equilibrium composition using standard equilibrium calculation methods at 525° C. Then to this composition, additional toluene was added and chemical equilibrium for the new system was calculated. In the newly equilibrated system the incremental toluene was converted to additional benzene and mixed xylenes. These calculations were done at two toluene additions representing 30% recycle and 50% recycle of the baseline toluene amounts. At 30% recycle, the corresponding toluene conversion was 14% of the added toluene; at 50% recycle the conversion was 22% of the added toluene. The molar selectivity in both cases was 50/50 benzene/xylenes.

[0044] Results are shown below in Table 1 (mass balance for 30% recycle) and Table 2 (mass balance for 50% recycle). The results demonstrate that there are no chemical equilibrium constraints to the present invention process to increase the yield of more valuable benzene and xylenes products. The values shown in the tables are kg/hour. In the tables, A=compound; B=reaction product without toluene recycle; C=equilibrated product without toluene recycle; D=toluene recycle; E=combined feed; F=equilibrated reaction product with toluene recycle; G=incremental production; and H=percent toluene conversion.

TABLE 1

A	B	C	D	E	F	G	H
Benzene	137	155		155	182	27	
Toluene	386	345	115	460	397		14
o-Xylene	44	74		74	84	10	
m-Xylene	120	146		146	164	18	
p-Xylene	92	59		59	67	8	
Total	779	779		894	894	63	

TABLE 2

A	B	C	D	E	F	G	H
Benzene	137	155		155	208	53	
Toluene	386	345	230	575	448		22
o-Xylene	44	74		74	94	20	
m-Xylene	120	146		146	184	38	
p-Xylene	92	59		59	75	16	
Total	779	779		1009	1009	127	

[0045] The results of this example show that a CFP process may be conducted to enhance benzene and xylenes production by way of the present process. It is a benefit of the present invention process that an existing CFP reactor and catalyst system in a fluid bed can be used in this manner. This avoids the need for a separate fixed bed disproportionation reactor system to increase production of benzene and xylenes. Another advantage of the present invention is that it allows manufacturing flexibility for the CFP process to respond to changes in product demand. For example, if xylene demand is high, more toluene can be recycled to the CFP reactor to produce more xylene. When toluene demand is high, the amount of recycle can be reduced or recycle can be stopped completely.

[0046] All patents, patent applications, test procedures, priority documents, articles, publications, manuals, and other documents cited herein are fully incorporated by reference to the extent such disclosure is not inconsistent with this invention and for all jurisdictions in which such incorporation is permitted.

[0047] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated.

[0048] While the illustrative embodiments of the invention have been described with particularity, it will be understood that various other modifications will be apparent to and may be readily made by those skilled in the art without departing from the spirit and scope of the invention. Accordingly, it is not intended that the scope of the claims hereof be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present invention, including all features which would be treated as equivalents thereof by those skilled in the art to which the invention pertains.

What is claimed is:

1. An improved catalytic fast pyrolysis process comprising steps of:

- a) feeding biomass, catalyst composition, and transport fluid to a catalytic fast pyrolysis process fluidized bed reactor maintained at reaction conditions to manufacture a raw fluid product stream,
- b) feeding the raw fluid product stream of step a) to a solids separation and stripping system to produce separated solids and a fluid product stream,
- c) feeding the fluid product stream of step b) to a vapor/liquid separation system to produce a liquid phase stream comprising components selected from the group consisting of water, char, coke, ash, catalyst fines and combinations thereof, and a vapor phase stream comprising benzene, toluene and xylenes,
- d) feeding the vapor phase stream of step c) to a product recovery system to recover benzene, toluene and xylenes, and

e) recycling at least a portion of the recovered toluene of step d) to the fluidized bed reactor of step a).

2. The process of claim 1 wherein the crystalline molecular sieve of the catalyst composition of step a) is characterized by a silica/alumina mole ratio greater than 12 and a Constraint Index from 1 to 12.

3. The process of claim 1 wherein the fluidized bed reaction conditions include a temperature of from 300 to 1000° C. and pressure from 100 to 1500 kPa.

4. The process of claim 2 wherein the crystalline molecular sieve of the catalyst composition of step a) is characterized by a silica/alumina mole ratio from greater than 12 to 240 and a Constraint Index from 5 to 10.

5. The process of claim 2 wherein the catalyst composition of step a) comprises a crystalline molecular sieve having the structure of ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-50 or combinations thereof.

6. The process of claim 4 wherein the catalyst composition of step a) comprises a crystalline molecular sieve having the structure of ZSM-5, ZSM-11, ZSM-22, ZSM-23 or combinations thereof.

7. The process of claim 5 wherein the catalyst composition of step a) comprises a crystalline molecular sieve having the structure of ZSM-5.

8. The process of claim 1 wherein from 5 to 99% of the recovered toluene of step d) is recycled to the fluidized bed reactor of step a).

9. The process of claim 8 wherein from 30 to 50% of the recovered toluene of step d) is recycled to the fluidized bed reactor of step a).

10. The process of claim 1 wherein the solids separation and stripping system of step b) comprises a cyclone or series of cyclones.

11. The process of claim 1 wherein the vapor/liquid separation system of step c) comprises venturi systems, quench systems, condensers, chillers, absorption systems, scrubbers, demisters, or combinations thereof.

12. The process of claim 1 wherein the product recovery system of step d) comprises condensers, chillers, absorption systems, demisters, or combinations thereof.

13. An improved catalytic fast pyrolysis process comprising steps of:

- a) feeding biomass, catalyst composition comprising a crystalline molecular sieve having the structure of ZSM-5, and transport fluid to a catalytic fast pyrolysis process fluidized bed reactor maintained at reaction conditions including a temperature from 300 to 1000° C., pressure from 100 to 1500 kPa and catalyst-to-biomass mass ratio of from 0.1 to 40 to manufacture a raw fluid product stream,
- b) feeding the raw fluid product stream of step a) to a solids separation and stripping system to produce separated solids and a fluid product stream,
- c) feeding the fluid product stream of step b) to a vapor/liquid separation system to produce a liquid phase stream comprising components selected from the group consisting of water, char, coke, ash, catalyst fines and combinations thereof, and a vapor phase stream comprising benzene, toluene and xylenes,
- d) feeding the vapor phase stream of step c) to a product recovery system to recover benzene, toluene and xylenes, and
- e) recycling from 5 to 99% of the recovered toluene of step d) to the fluidized bed reactor of step a).

14. The process of claim **13** wherein the catalyst composition comprises binder material selected from the group consisting of porous inorganic oxide, clay or combinations thereof.

15. The process of claim **14** wherein the inorganic oxide comprises alumina, zirconia, silica, magnesia, thoria, titania, boria or combinations thereof.

16. The process of claim **14** wherein the clay comprises bentonite, kieselguhr or combinations thereof.

17. The process of claim **13** wherein from 30 to 50% of the recovered toluene of step d) is recycled to the fluidized bed reactor of step a).

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