



(51) International Patent Classification:

C07C 5/09 (2006.01) C07C 15/04 (2006.01)
C07C 11/04 (2006.01) C07C 11/24 (2006.01)
C07C 2/48 (2006.01)

(21) International Application Number:

PCT/US2018/012064

(22) International Filing Date:

02 January 2018 (02.01.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/442,248 04 January 2017 (04.01.2017) US

(71) Applicant: SABIC GLOBAL TECHNOLOGIES, B.V.
[NL/NL]; Plasticslaan 1, 4612PX Bergen op Zoom (NL).

(72) Inventors; and

(71) Applicants (for US only): SANKARANARAYANAN, Krishnan [NL/US]; 19 Heights Creek Drive, Missouri City, Texas 77459 (US). GAUTAM, Pankaj S. [IN/US]; 239 Needleleaf Lane, Sugar Land, Texas 77479 (US). MAMEDOV, Aghaddin [AZ/US]; 5714 Kendal Hill Lane, Sugar Land, Texas 77479 (US). PANNALA, Sreekanth [US/US]; 5907 Quiet Point Lane, Sugar Land, Texas 77479

(US). NAIR, Balamurali [IN/US]; 5410 Valley Country Lane, Sugar Land, Texas 77479 (US).

(74) Agent: CONLEY ROSE, P.C. et al.; 5601 Granite Parkway, Suite 500, Plano, Texas 75024 (US).

(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, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, 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, SA, 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, ST, 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).

(54) Title: AN INTEGRATED PROCESS FOR CONVERSION OF METHANE TO ETHYLENE AND BENZENE

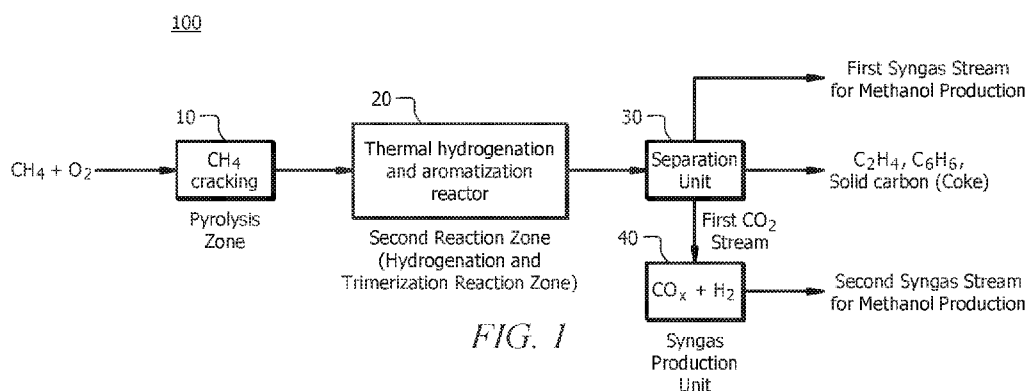


FIG. 1

(57) Abstract: A process for producing ethylene and benzene comprising introducing fuel and oxidant to combustion zone to produce combustion product; introducing first reactant mixture comprising hydrocarbons and combustion product to first reaction zone, wherein combustion product heats hydrocarbons to temperature effective for pyrolysis; allowing first reactant mixture to react via pyrolysis and produce pyrolysis product comprising unconverted hydrocarbons, C₂H₂, C₂H₄, CO, H₂, H₂O, and CO₂; cooling pyrolysis product in quench zone to form cooled pyrolysis product; introducing cooled pyrolysis product to second reaction zone; allowing a first portion of acetylene in cooled pyrolysis product to undergo hydrogenation to ethylene and a second portion of acetylene in cooled pyrolysis product to undergo trimerization to benzene, to produce second zone effluent comprising unconverted hydrocarbons, unconverted C₂H₂, C₂H₄, C₆H₆, CO, H₂, H₂O, and CO₂; and separating second zone effluent into ethylene, benzene, CO₂, and syngas.



Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

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))*

AN INTEGRATED PROCESS FOR CONVERSION OF METHANE TO ETHYLENE AND BENZENE

TECHNICAL FIELD

[0001] The present disclosure relates to methods of producing olefins and aromatic hydrocarbons, more specifically methods of producing ethylene and benzene by integrating hydrocarbon pyrolysis with ethylene and benzene production.

BACKGROUND

[0002] Hydrocarbons, and specifically olefins such as ethylene, can be typically used to produce a wide range of products, for example, break-resistant containers and packaging materials. Currently, for industrial scale applications, ethylene is produced by heating natural gas condensates and petroleum distillates, which include ethane and higher hydrocarbons, and the produced ethylene is separated from a product mixture by using gas separation processes.

[0003] Benzene is an important chemical, with applications ranging from chemical intermediates to solvents. Benzene is a natural constituent of crude oil and it is used primarily as a precursor for manufacturing chemicals with more complex structure, such as cyclohexane, nitrobenzene, xylenes, ethylbenzene, cumene, and other various alkylbenzenes. Benzene also has a high octane number, and as such is an important component of gasoline. Benzene can also be used for making some types of rubbers, lubricants, dyes, detergents, drugs, explosives, and pesticides. However, there is concern over the depletion of finite reserves of crude oil. Thus, there is an ongoing need for the development of processes for the production of olefins such as ethylene, and aromatic hydrocarbons such as benzene.

BRIEF SUMMARY

[0004] Disclosed herein is a process for producing ethylene and benzene comprising (a) introducing a fuel gas stream and an oxidant gas to a combustion zone to produce a combustion product, (b) introducing a first reactant mixture to a first reaction zone, wherein the first reactant mixture comprises a hydrocarbon stream and at least a portion of the combustion product, and wherein the combustion product heats the hydrocarbon stream to a first temperature effective for a pyrolysis reaction, (c) allowing at least a portion of the first reactant mixture to react via the pyrolysis reaction and produce a pyrolysis reaction product, wherein the pyrolysis reaction product comprises unconverted hydrocarbons, acetylene (C_2H_2), ethylene (C_2H_4), carbon monoxide (CO),

hydrogen (H_2), water (H_2O), and carbon dioxide (CO_2), (d) cooling at least a portion of the pyrolysis reaction product in a quench zone to form a cooled pyrolysis reaction product, wherein the cooled pyrolysis reaction product is characterized by a second temperature, and wherein the second temperature is lower than the first temperature, (e) introducing the cooled pyrolysis reaction product to a second reaction zone, (f) allowing a first portion of the acetylene in the cooled pyrolysis reaction product to undergo hydrogenation to ethylene and a second portion of the acetylene in the cooled pyrolysis reaction product to undergo trimerization to benzene, to produce a second reaction zone effluent, wherein the second reaction zone effluent comprises unconverted hydrocarbons, unconverted C_2H_2 , C_2H_4 , benzene (C_6H_6), CO , H_2 , H_2O , and CO_2 , and wherein an amount of C_2H_4 in the second reaction zone effluent is greater than an amount of C_2H_4 in the cooled pyrolysis reaction product, and (g) separating at least a portion of the second reaction zone effluent into an ethylene stream, a benzene stream, a first CO_2 stream, and a first syngas stream, wherein the first syngas stream comprises H_2 and CO .

[0005] Also disclosed herein is a process for producing ethylene and benzene comprising (a) introducing a fuel gas stream and an oxidant gas to a combustion zone to produce a combustion product, (b) introducing a first reactant mixture to a first reaction zone, wherein the first reactant mixture comprises a hydrocarbon stream and at least a portion of the combustion product, and wherein the combustion product heats the hydrocarbon stream to a first temperature effective for a pyrolysis reaction, wherein the first temperature is equal to or greater than about $2,000^\circ\text{C}$, (c) allowing at least a portion of the first reactant mixture to react via the pyrolysis reaction and produce a pyrolysis reaction product, wherein the pyrolysis reaction product comprises unconverted hydrocarbons, acetylene (C_2H_2), ethylene (C_2H_4), carbon monoxide (CO), hydrogen (H_2), water (H_2O), and carbon dioxide (CO_2), (d) cooling at least a portion of the pyrolysis reaction product in a quench zone to form a cooled pyrolysis reaction product, wherein a first reactor comprises the combustion zone, the first reaction zone, and the quench zone, (e) introducing the cooled pyrolysis reaction product to a second reaction zone, (f) allowing a first portion of the acetylene in the cooled pyrolysis reaction product to undergo hydrogenation to ethylene and a second portion of the acetylene in the cooled pyrolysis reaction product to undergo trimerization to benzene at a temperature of from about 850°C to about 950°C effective for acetylene hydrogenation to ethylene and/or acetylene trimerization to benzene (C_6H_6), to produce a second reaction zone effluent, wherein the second reaction zone effluent comprises unconverted

hydrocarbons, unconverted C_2H_2 , C_2H_4 , C_6H_6 , CO, H_2 , H_2O , and CO_2 ; wherein an amount of C_2H_4 in the second reaction zone effluent is greater than an amount of C_2H_4 in the cooled pyrolysis reaction product; wherein a second reactor comprises the second reaction zone; wherein the second reactor comprises a glass lined reactor, a quartz lined reactor, a ceramic lined reactor, or combinations thereof; and wherein the second reaction zone comprises thermally conductive material particles, wherein the thermally conductive material particles are non-metallic and/or have non-metallic surfaces, and wherein coke is deposited on the thermally conductive material particles during step (f) to produce spent thermally conductive material particles, (g) separating at least a portion of the second reaction zone effluent into an ethylene stream, a benzene stream, a first CO_2 stream, a first syngas stream, and coke, wherein the first syngas stream comprises H_2 and CO, (h) regenerating at least a portion of the spent thermally conductive material particles to produce the thermally conductive material particles and a second CO_2 stream, (i) contacting at least a portion of the first CO_2 stream and/or at least a portion of the second CO_2 stream with hydrogen to produce a second syngas stream comprising H_2 and CO, and (j) introducing at least a portion of the first syngas stream and/or at least a portion of the second syngas stream a third reaction zone comprising a catalyst to produce a methanol stream.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] For a detailed description of the preferred aspects of the disclosed methods, reference will now be made to the accompanying drawing in which:

[0007] Figure 1 displays a schematic of an ethylene and benzene production system;

[0008] Figure 2 displays a schematic of a reactor for the conversion of acetylene to ethylene and benzene;

[0009] Figure 3 displays another schematic of a reactor for the conversion of acetylene to ethylene and benzene;

[0010] Figure 4 displays yet another schematic of a reactor for the conversion of acetylene to ethylene and benzene; and

[0011] Figure 5 displays still yet another schematic of a reactor for the conversion of acetylene to ethylene and benzene.

DETAILED DESCRIPTION

[0012] Disclosed herein are methods for producing ethylene and benzene comprising (a) introducing a fuel gas stream and an oxidant gas to a combustion zone to produce a combustion

product; (b) introducing a first reactant mixture to a first reaction zone, wherein the first reactant mixture comprises a hydrocarbon stream and at least a portion of the combustion product, and wherein the combustion product heats the hydrocarbon stream to a first temperature effective for a pyrolysis reaction; (c) allowing at least a portion of the first reactant mixture to react via the pyrolysis reaction and produce a pyrolysis reaction product, wherein the pyrolysis reaction product comprises unconverted hydrocarbons, acetylene (C_2H_2), ethylene (C_2H_4), carbon monoxide (CO), hydrogen (H_2), water (H_2O), and carbon dioxide (CO_2); (d) cooling at least a portion of the pyrolysis reaction product in a quench zone to form a cooled pyrolysis reaction product, wherein the cooled pyrolysis reaction product is characterized by a second temperature, and wherein the second temperature is lower than the first temperature; (e) introducing the cooled pyrolysis reaction product to a second reaction zone; (f) allowing a first portion of the acetylene in the cooled pyrolysis reaction product to undergo hydrogenation to ethylene and a second portion of the acetylene in the cooled pyrolysis reaction product to undergo trimerization to benzene, to produce a second reaction zone effluent, wherein the second reaction zone effluent comprises unconverted hydrocarbons, unconverted C_2H_2 , C_2H_4 , benzene (C_6H_6), CO, H_2 , H_2O , and CO_2 ; and wherein an amount of C_2H_4 in the second reaction zone effluent is greater than an amount of C_2H_4 in the cooled pyrolysis reaction product; and (g) separating at least a portion of the second reaction zone effluent into an ethylene stream, a benzene stream, a first CO_2 stream, and a first syngas stream, wherein the first syngas stream comprises H_2 and CO. The second temperature is a temperature effective for acetylene hydrogenation to ethylene and/or acetylene trimerization to C_6H_6 . At least a portion of the first CO_2 stream can be fed to a syngas production unit to produce a second syngas stream. In some aspects, at least a portion of the first syngas stream and/or at least a portion of the second syngas stream can be used for methanol production.

[0013] Other than in the operating examples or where otherwise indicated, all numbers or expressions referring to quantities of ingredients, reaction conditions, and the like, used in the specification and claims are to be understood as modified in all instances by the term “about.” Various numerical ranges are disclosed herein. Because these ranges are continuous, they include every value between the minimum and maximum values. The endpoints of all ranges reciting the same characteristic or component are independently combinable and inclusive of the recited endpoint. Unless expressly indicated otherwise, the various numerical ranges specified in this application are approximations. The endpoints of all ranges directed to the same component or

property are inclusive of the endpoint and independently combinable. The term “from more than 0 to an amount” means that the named component is present in some amount more than 0, and up to and including the higher named amount.

[0014] The terms “a,” “an,” and “the” do not denote a limitation of quantity, but rather denote the presence of at least one of the referenced item. As used herein the singular forms “a,” “an,” and “the” include plural referents.

[0015] As used herein, “combinations thereof” is inclusive of one or more of the recited elements, optionally together with a like element not recited, e.g., inclusive of a combination of one or more of the named components, optionally with one or more other components not specifically named that have essentially the same function. As used herein, the term “combination” is inclusive of blends, mixtures, alloys, reaction products, and the like.

[0016] Reference throughout the specification to “an aspect,” “another aspect,” “other aspects,” “some aspects,” and so forth, means that a particular element (e.g., feature, structure, property, and/or characteristic) described in connection with the aspect is included in at least an aspect described herein, and may or may not be present in other aspects. In addition, it is to be understood that the described element(s) can be combined in any suitable manner in the various aspects.

[0017] As used herein, the terms “inhibiting” or “reducing” or “preventing” or “avoiding” or any variation of these terms, include any measurable decrease or complete inhibition to achieve a desired result.

[0018] As used herein, the term “effective,” means adequate to accomplish a desired, expected, or intended result.

[0019] As used herein, the terms “comprising” (and any form of comprising, such as “comprise” and “comprises”), “having” (and any form of having, such as “have” and “has”), “including” (and any form of including, such as “include” and “includes”) or “containing” (and any form of containing, such as “contain” and “contains”) are inclusive or open-ended and do not exclude additional, unrecited elements or method steps.

[0020] Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art.

[0021] Compounds are described herein using standard nomenclature. For example, any position not substituted by any indicated group is understood to have its valency filled by a bond as

indicated, or a hydrogen atom. A dash (“-”) that is not between two letters or symbols is used to indicate a point of attachment for a substituent. For example, -CHO is attached through the carbon of the carbonyl group.

[0022] Referring to Figure 1, an ethylene and benzene production system 100 is disclosed. The ethylene and benzene production system 100 generally comprises a pyrolysis zone 10 for methane (CH₄) cracking (e.g., combustion zone; first reaction zone; quenching zone); a second reaction zone 20 for the selective thermal hydrogenation of acetylene to ethylene and for the trimerization of acetylene to benzene (e.g., hydrogenation and trimerization reaction zone); a separation unit 30 for the recovery of ethylene, benzene and syngas (e.g., a first syngas stream); and a syngas production unit 40 for the hydrogenation of carbon dioxide (e.g., first CO₂ stream and/or second CO₂ stream) to carbon monoxide. As will be appreciated by one of skill in the art, and with the help of this disclosure, ethylene and benzene production system components shown in Figure 1 can be in fluid communication with each other (as represented by the connecting lines indicating a direction of fluid flow) through any suitable conduits (e.g., pipes, streams, etc.).

[0023] The pyrolysis zone 10 can comprise a combustion zone and a first reaction zone. Impurities and contaminants can be removed from a fuel gas stream and/or a hydrocarbon stream prior to introducing to the combustion zone and/or the first reaction zone, respectively. In some aspects, the fuel gas stream and the hydrocarbon stream can be the same (e.g., can comprise the same hydrocarbons, for example can be portions of the same gas stream feedstock). In other aspects, the fuel gas stream and the hydrocarbon stream can be the different (e.g., can comprise different hydrocarbons, for example originating from different upstream sources).

[0024] The fuel gas stream and/or the hydrocarbon stream can comprise methane, ethane, propane, natural gas, natural gas liquids, associated gas, well head gas, enriched gas, heavy hydrocarbons, petcoke, naphtha, heavy oil, heavy oil residue, and the like, or combinations thereof. Generally, natural gas is a naturally occurring hydrocarbon gas mixture comprising mostly methane, but commonly including varying amounts of other higher alkanes, and sometimes a small percentage of carbon dioxide, nitrogen, hydrogen sulfide, helium, etc. Heavy oil residues generally comprise polyalkylbenzenes such as polyethylbenzenes (PEBs), and well as multi-ring compounds. Petcoke generally refers to a carbonaceous solid produced in oil refinery coker units or other cracking processes. Heavy hydrocarbons generally comprise hydrocarbons which are solid or extremely viscous at standard processing conditions, and can include materials such as, but not

limited to, asphaltenes, tars, paraffin waxes, coke, refining residues, and other similar residual hydrocarbon materials. Heavy hydrocarbons can include any material that comprises a majority of hydrocarbon materials with a molecular weight range of about 700 to 2,000,000 Daltons. Heavy oil generally refers to heavy crude, oils sands bitumen, bottom of the barrel and residue left over from refinery processes (e.g., visbreaker bottoms), and any other lower quality material that contains a substantial quantity of high boiling hydrocarbon fractions (e.g., that boil at or above 343°C, or alternatively at or above about 524°C). Nonlimiting examples of heavy oil feedstocks include, but are not limited to, Lloydminster heavy oil, Cold Lake bitumen, Athabasca bitumen, atmospheric tower bottoms, vacuum tower bottoms, residuum (or “resid”), resid pitch, vacuum residue, and nonvolatile liquid fractions that remain after subjecting crude oil, bitumen from tar sands, liquefied coal, oil shale, or coal tar feedstocks to distillation, hot separation, and the like; and that contain higher boiling fractions and/or asphaltenes. Naptha generally comprises flammable liquid hydrocarbon mixtures.

[0025] In an aspect, a process for producing ethylene and benzene as disclosed herein can comprise a step of introducing the fuel gas stream and an oxidant gas to the combustion zone to produce a combustion product. The combustion zone can comprise a burner, such as an in-line burner; a furnace; or combinations thereof; wherein the fuel gas stream is burned (e.g., combusted) with the oxidant gas to produce the combustion product. The oxidant gas can comprise oxygen, purified oxygen, air, oxygen-enriched air, and the like, or combinations thereof. In some aspects, the oxidant gas is oxygen-enriched, such as oxygen-enriched air, to minimize NO_x production in the combustion zone. As will be appreciated by one of skill in the art, and with the help of this disclosure, NO_x products can be acidic and as such would necessitate downstream removal. Water or steam can be further introduced to the combustion zone to lower and thereby control the combustion product temperature. The combustion product generally comprises combustion products, such as carbon monoxide (CO), CO₂, water (H₂O), as well as some unconverted hydrocarbons (e.g., hydrocarbons that were present in the fuel gas stream and did not combust). Depending on the configuration of the pyrolysis zone 10, the combustion product may not be isolatable, and it might be introduced as produced to the first reaction zone.

[0026] In an aspect, a process for producing ethylene and benzene as disclosed herein can comprise introducing a first reactant mixture to the first reaction zone, wherein the first reactant mixture comprises the hydrocarbon stream and at least a portion of the combustion product, and

wherein the combustion product heats the hydrocarbon stream to a first temperature effective for a pyrolysis reaction; and allowing at least a portion of the first reactant mixture to react via the pyrolysis reaction and produce a pyrolysis reaction product. The pyrolysis reaction product can comprise unconverted hydrocarbons, acetylene, ethylene, CO, H₂, water, and CO₂.

[0027] The first reaction zone excludes the catalyst. As will be appreciated by one of skill in the art, and with the help of this disclosure, while there are catalytic processes for hydrocarbon pyrolysis (e.g., methane pyrolysis), the current disclosure does not utilize a catalyst for hydrocarbon pyrolysis; the hydrocarbon pyrolysis as disclosed herein is thermal in contrast to catalyzed.

[0028] In some aspects, the pyrolysis zone 10 can comprise a reactor (e.g., a first reactor) that contains both the combustion zone and the first reaction zone. In other aspects, the pyrolysis zone 10 can comprise a furnace that contains the combustion zone; and a reactor (e.g., a first reactor) that contains the first reaction zone and is configured to receive the combustion product from the furnace comprising the combustion zone. A diluent such as an inert gas (e.g., nitrogen, argon, helium, etc.) and/or steam can be further introduced to the first reaction zone.

[0029] The hydrocarbon stream can be further pre-heated in pre-heaters (e.g., electrical heaters, heat exchangers, etc.) before being heated to the first temperature (e.g., temperature effective for the pyrolysis reaction) by direct heat exchange through contact with the combustion product. A temperature of the combustion product can be a temperature effective to reach a pyrolysis reaction temperature (e.g., first temperature, first reaction zone temperature) of equal to or greater than about 1,000 °C, alternatively equal to or greater than about 1,500 °C, alternatively equal to or greater than about 2,000 °C, alternatively equal to or greater than about 2,250 °C, alternatively from about 1,000 °C to about 2,500 °C, alternatively from about 1,500 °C to about 2,500 °C, or alternatively from about 2,000 °C to about 2,500 °C. As will be appreciated by one of skill in the art, and with the help of this disclosure, higher temperatures in the first reaction zone favor alkyne (e.g., acetylene) formation, while lower temperatures in the first reaction zone favor olefin or alkene (e.g., ethylene) formation.

[0030] In an aspect, the first reaction zone can be characterized by a residence time effective to allow for the conversion of at least a portion of the first reactant mixture to acetylene and ethylene. The first reaction zone can be characterized by a residence time of from about 0.1 milliseconds

(ms) to 100 ms, alternatively from about 0.5 ms to about 80 ms, or alternatively from about 1 ms to about 50 ms.

[0031] Suppression or reduction of reactions leading to products other than the desired products (e.g., alkynes, acetylene, olefins, ethylene) may be required to achieve the desired products. This may be accomplished by adjusting the reaction temperature, pressure, and/or quenching after a desired residence time. In some aspects, the hydrocarbon stream that is introduced to the first reaction zone can be characterized by a pressure of from about 1 bar to about 20 bar (e.g., from about 100 kPa to about 2,000 kPa), to achieve the desired products.

[0032] The pyrolysis zone 10 can be designed to accommodate one or more gas feed streams (e.g., fuel gas stream, hydrocarbon stream), which may employ natural gas combined with other gas components including, but not limited to hydrogen, carbon monoxide, carbon dioxide, ethane, and ethylene. The pyrolysis zone 10 can be designed to accommodate one or more oxidant gas streams, such as an oxygen stream and an oxygen-containing stream, for example an air stream, which employ unequal oxidant concentrations for purposes of temperature or composition control. As will be appreciated by one of skill in the art, and with the help of this disclosure, the pyrolysis zone 10 may comprise a single device or multiple devices. Each device of the pyrolysis zone 10 may comprise one or more sections. Products from the combustion zone are communicated to the first reaction zone via the combustion product stream. Depending on the type and configuration of the pyrolysis zone 10 used, the combustion product stream may not be isolatable (for example, in configurations where the combustion zone and the first reaction zone are contained within a common vessel or reactor).

[0033] In an aspect, a process for producing ethylene and benzene as disclosed herein can comprise cooling at least a portion of the pyrolysis reaction product in a quench zone to form a cooled pyrolysis reaction product, wherein the cooled pyrolysis reaction product is characterized by a second temperature, and wherein the second temperature is lower than the first temperature.

[0034] In some aspects, to stop pyrolysis reactions occurring in the first reaction zone, prevent undesired reverse reactions, or prevent further reactions that form carbon and hydrocarbon compounds other than the desired products, rapid cooling or “quenching” of pyrolysis reaction products can be employed. In an aspect, the pyrolysis zone 10 can further comprise a quench zone, wherein the pyrolysis reaction products are quenched prior to exiting the pyrolysis unit 10 via the cooled pyrolysis reaction product. The quench zone can employ any suitable quenching methods,

for example spraying a quench fluid such as steam, water, oil, or liquid product into a reactor quench zone or chamber; conveying the product stream through or into water, natural gas feed, or liquid products; preheating other streams such as fuel gas stream and/or hydrocarbon stream; generating steam; expanding in a kinetic energy quench, such as a Joule Thompson expander, choke nozzle, turbo expander, etc.; or combinations thereof. As will be appreciated by one of skill in the art, and with the help of this disclosure, the quench zone may be incorporated within a pyrolysis reactor (e.g., a first reactor), may comprise a separate vessel or device from the pyrolysis reactor, or both. Pyrolysis units for the production of acetylene and ethylene from hydrocarbons are described in more detail in U.S. Patent Nos. 5,824,834; 5,789,644; and 8,445,739; and U.S. Patent Application No. 2010/0167134 A1; each of which is incorporated by reference herein in its entirety.

[0035] The cooled pyrolysis reaction product can comprise unconverted hydrocarbons, acetylene, ethylene, CO, H₂, water (H₂O), and CO₂. As will be appreciated by one of skill in the art, and with the help of this disclosure, water produced in the combustion zone can react with methane to produce syngas.

[0036] In an aspect, a first reactor can comprise the first reaction zone. In some aspects, the first reactor can further comprise the combustion zone, the quench zone, or both the combustion zone and the quench zone. In such aspects, the pyrolysis zone 10 can comprise the first reactor comprising the combustion zone, the first reaction zone, and the quench zone.

[0037] In an aspect, a process for producing ethylene and benzene as disclosed herein can comprise introducing the cooled pyrolysis reaction product to the second reaction zone 20 (e.g., hydrogenation and trimerization reaction zone); and allowing a first portion of the acetylene in the cooled pyrolysis reaction product to undergo hydrogenation to ethylene and a second portion of the acetylene in the cooled pyrolysis reaction product to undergo trimerization to benzene, to produce a second reaction zone effluent, wherein the second reaction zone effluent comprises unconverted hydrocarbons, unconverted C₂H₂, C₂H₄, benzene (C₆H₆), CO, H₂, H₂O, and CO₂; and wherein an amount of C₂H₄ in the second reaction zone effluent is greater than an amount of C₂H₄ in the cooled pyrolysis reaction product.

[0038] In some aspects, the cooled pyrolysis reaction product that is introduced to the second reaction zone 20 can comprise (i) acetylene in an amount of from about 5 vol.% to about 30 vol.%, alternatively from about 10 vol.% to about 25 vol.%, or alternatively from about 13 vol.% to about

18 vol.%, based on the total volume of the cooled pyrolysis reaction product; (ii) hydrogen in an amount of from about 10 vol.% to about 70 vol.%, alternatively from about 40 vol.% to about 70 vol.%, or alternatively from about 45 vol.% to about 60 vol.%, based on the total volume of the cooled pyrolysis reaction product; (iii) methane (e.g., unconverted methane from pyrolysis) in an amount of from about 5 vol.% to about 30 vol.%, alternatively from about 10 vol.% to about 25 vol.%, or alternatively from about 13 vol.% to about 18 vol.%, based on the total volume of the cooled pyrolysis reaction product; and (iv) carbon dioxide in an amount of from about 5 vol.% to about 30 vol.%, alternatively from about 10 vol.% to about 25 vol.%, or alternatively from about 15 vol.% to about 25 vol.%, based on the total volume of the cooled pyrolysis reaction product. As will be appreciated by one of skill in the art, and with the help of this disclosure, the composition of the cooled pyrolysis reaction product might need to be adjusted to meet the optimum composition for being introduced to the second reaction zone 20.

[0039] In an aspect, the second reaction zone 20 can be characterized by the second temperature, wherein the second temperature is a temperature effective for acetylene hydrogenation to ethylene and/or acetylene trimerization to C_6H_6 . In an aspect, the second temperature can be from about 600 °C to about 1,000 °C, alternatively from about 750 °C to about 975 °C, or alternatively from about 850 °C to about 950 °C.

[0040] In an aspect, the second reaction zone 20 excludes a catalyst. As will be appreciated by one of skill in the art, and with the help of this disclosure, while there are catalytic processes for conversion of acetylene to ethylene (e.g., liquid phase hydrogenation of acetylene to ethylene, in the presence of a catalyst, such as palladium (Pd), for example), as well as catalytic processes for conversion of acetylene to benzene, the current disclosure does not utilize a catalyst for the conversion of acetylene to ethylene and/or benzene; the conversion of acetylene to ethylene and/or benzene as disclosed herein is thermal in contrast to catalyzed. In an aspect, the second reaction zone 20 excludes liquid phase hydrogenation of acetylene to ethylene. In an aspect, the entire contents of the second reaction zone 20 are in gas phase (e.g., 100% gas phase reaction zone).

[0041] The second reaction zone 20 employs the simultaneous production of benzene and ethylene by thermal conversion of acetylene in a non-metallic reactor, which in some configurations can be a tubular reactor. The thermal conversion of acetylene with simultaneous production of benzene and ethylene can occur in the presence of one or more non-metallic surfaces, wherein the one or more non-metallic surfaces can comprise inner reactor walls or

surfaces, reactor packing material surfaces (e.g., thermally conductive material particles surfaces), and the like, or combinations thereof.

[0042] In an aspect, the second reaction zone 20 is contained in a non-metallic reactor, such as a glass-lined reactor, a quartz-lined reactor, or a ceramic-lined reactor. In an aspect, the second reaction zone is defined by non-metallic boundaries, such as one or more glass boundaries, one or more quartz boundaries, one or more ceramic boundaries, and the like, or combinations thereof. As will be appreciated by one of skill in the art, and with the help of this disclosure, in metallic reactors, acetylene conversion undesirably proceeds in the direction of a deep decomposition of acetylene with formation of hydrogen and coke fragments.

[0043] In some aspects, a common reactor can comprise both the first reaction zone and the second reaction zone 20. In such aspects, the common reactor can have an inner common reactor surface, wherein at least a portion of the inner common reactor surface contacts the cooled pyrolysis reaction product, and wherein at least a portion of the inner common reactor surface is non-metallic. In configurations where a common reactor is used for containing both the first reaction zone and the second reaction zone, the portion of the common reactor that contains the second reaction zone has an inner surface (e.g., inner common reactor surface) that is non-metallic, for example glass, quartz, ceramic, and the like, or combinations thereof. In configurations where a common reactor is used for containing both the first reaction zone and the second reaction zone, at least the portion of the common reactor that contains the second reaction zone can be lined with glass, quartz, ceramic, and the like, or combinations thereof, to provide for a non-metallic inner common reactor surface. The common reactor that comprises both the first reaction zone and the second reaction zone can further comprise the quench zone and optionally the combustion zone. The common reactor can be an autothermal reactor.

[0044] In other aspects, the first reactor can comprise the first reaction zone, and a second reactor can comprise the second reaction zone 20. In such aspects, the second reactor can have an inner second reactor surface, wherein at least a portion of the inner second reactor surface contacts the cooled pyrolysis reaction product, and wherein the inner second reactor surface is non-metallic, for example glass, quartz, ceramic, and the like, or combinations thereof. The second reactor can be an autothermal reactor.

[0045] In an aspect, the second reaction zone 20 can comprise a reactor packing material, wherein the reactor packing material is non-metallic and/or has non-metallic surfaces. The reactor

packing material can be of any suitable size or shape to provide a desired effective surface area, fluid flow characteristics, heat exchange, and the like. The reactor packing material can be part of a fixed bed of a fluidized bed in the second reaction zone 20. The reactor packing material can have any suitable size or shape, such as fibers, filaments, particles, spheres, pellets, rods, cylinders, trilobes, quadralobes, and the like, or combinations thereof.

[0046] In an aspect, the reactor packing material can comprise thermally conductive material particles, wherein the thermally conductive material particles are non-metallic and/or have non-metallic surfaces. The thermally conductive material particles can be glass particles, quartz particles, ceramic particles, and the like, or combinations thereof. The thermally conductive material particles can have surfaces that are coated with non-metallic materials (e.g., glass, quartz, ceramic, and the like, or combinations thereof), such as glass-coated particles, quartz-coated particles, ceramic-coated particles, and the like, or combinations thereof.

[0047] As will be appreciated by one of skill in the art, and with the help of this disclosure, while the production of coke in the second reaction zone is minimized by the use of non-metallic surfaces, some coke will still be produced in the second reaction zone. Such coke can get deposited on the thermally conductive material particles to produce spent thermally conductive material particles. In an aspect, at least a portion of the spent thermally conductive material particles is regenerated to produce the thermally conductive material particles and a second CO₂ stream. In an aspect, the spent thermally conductive material particles can be regenerated by (i) removing at least a portion of the spent thermally conductive material particles from the second reaction zone; (ii) burning the coke off the at least a portion of the spent thermally conductive material particles in an oxidant gas, thereby producing the thermally conductive material particles (e.g., regenerated thermally conductive material particles) and the second CO₂ stream; and (iii) reintroducing at least a portion of the regenerated thermally conductive material particles to the second reaction zone. In such aspect, the second reaction zone can be contained in a riser type reactor with an outer thermally conductive material particles regeneration flow or circulation loop such as shown in Figure 5.

[0048] In some aspects, the second reaction zone can be characterized by a space velocity of from about 400 h⁻¹ to about 5,000 h⁻¹, or alternatively from about 1,800 h⁻¹ to about 3,000 h⁻¹. As will be appreciated by one of skill in the art, and with the help of this disclosure, the space velocity is an important factor affecting the benzene/ethylene ratio in the second reaction zone effluent,

wherein a high space velocity gives a high ethylene yield, while a low space velocity gives a high benzene yield.

[0049] In an aspect, a process for producing ethylene and benzene as disclosed herein can comprise separating in separation unit 30 at least a portion of the second reaction zone effluent into an ethylene stream, a benzene stream, a first CO₂ stream, and a first syngas stream, wherein the first syngas stream comprises H₂ and CO. The first syngas stream can be characterized by a H₂/CO molar ratio of from about 1:1 to about 2:1, alternatively from about 1.1:1 to about 1.95:1, or alternatively from about 1.2:1 to about 1.9:1. In some aspects, the separation unit 30 can employ distillation and/or cryogenic distillation to produce the ethylene stream, the benzene stream, and the first syngas stream.

[0050] In an aspect, at least a portion of the first CO₂ stream and/or at least a portion of the second CO₂ stream can be contacted with hydrogen in a syngas production unit 40 to produce a second syngas stream comprising H₂ and CO. The second syngas stream can be characterized by a H₂/CO molar ratio of from about 1:1 to about 2:1, alternatively from about 1.1:1 to about 1.95:1, or alternatively from about 1.2:1 to about 1.9:1. CO₂ can be converted to syngas by using a hydrogenating agent, e.g., hydrogen or any suitable compound that can provide hydrogen for hydrogenation reaction. Hydrogenation of CO₂ to syngas composition can be described by reactions (1)-(3):



wherein reaction (1) is an equilibrium controlled reaction which depends on the H₂/CO₂ ratio, as it can be seen from reactions (2) and (3). A catalyst for CO₂ hydrogenation to syngas can comprise mixed oxides of redox types, for example Cr, Fe, Mn, or Cu based oxides. In some aspects, the hydrogenation of carbon dioxide to syngas can be conducted in the presence of a CATOFIN catalyst, which is a chromium (Cr) based catalyst commercially available from Clariant, wherein the resulting syngas composition is suitable for methanol and/or olefins synthesis. As will be appreciated by one of skill in the art, and with the help of this disclosure, the composition of syngas produced by CO₂ hydrogenation is dependent upon the H₂/CO₂ ratio and on the CO₂ hydrogenation temperature.

[0051] In some aspects, at least a portion of the first syngas stream and/or at least a portion of the second syngas stream can be introduced to a third reaction zone (e.g., methanol production unit) comprising a catalyst to produce a methanol stream. A feed stream to the third reaction zone can be characterized by a H_2/CO molar ratio of about 2:1, alternatively about 2.1:1, alternatively from about 1.5:1 to about 2.5:1, alternatively from about 1.8:1 to about 2.3:1, or alternatively from about 2.0:1 to about 2.1:1. The H_2/CO molar ratio of the feed stream to the third reaction zone can be adjusted as necessary to meet the requirements of the methanol production unit, for example by varying a ratio of the first syngas stream to the second syngas stream; by subjecting the first syngas stream and/or the second syngas stream to a water-gas shift reaction; and the like; or combinations thereof. Generally, the water-gas shift reaction describes the catalytic reaction of carbon monoxide and water vapor to form carbon dioxide and hydrogen according to the reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$. Typically, the water-gas shift reaction is used to increase the H_2/CO molar ratio of gas streams comprising carbon monoxide and hydrogen (e.g., syngas streams). Water-gas shift catalysts can comprise any suitable water-gas shift catalysts, such as commercial water-gas shift catalysts; chromium or copper promoted iron-based catalysts; copper-zinc-aluminum catalyst; and the like; or combinations thereof. Alternatively, the H_2/CO molar ratio of the second syngas stream can be increased by increasing the amount of hydrogen introduced to the syngas production unit 40, as shown in reactions (2) and (3).

[0052] The methanol production unit can comprise any reactor suitable for a methanol synthesis reaction from CO and H_2 , such as for example an isothermal reactor, an adiabatic reactor, a slurry reactor, a cooled multi tubular reactor, and the like, or combinations thereof.

[0053] In an aspect, at least a portion of the CO and at least a portion of the H_2 of a feed stream to the methanol production unit (e.g., at least a portion of the first gas stream and/or at least a portion of the second gas stream) can undergo a methanol synthesis reaction. Generally, CO and H_2 can be converted into methanol (CH_3OH) according to reaction $CO + 2H_2 = CH_3OH$. Methanol synthesis from CO and H_2 is a catalytic process, and is most often conducted in the presence of copper based catalysts. The third reaction zone can comprise a catalyst, such as any suitable commercial catalyst used for methanol synthesis. Nonlimiting examples of catalysts suitable for use in the methanol production unit in the current disclosure include Cu, Cu/ZnO, Cu/ThO₂, Cu/Zn/Al₂O₃, Cu/ZnO/Al₂O₃, Cu/Zr, and the like, or combinations thereof.

[0054] In some aspects, coke can be further separated from the second reaction zone effluent, for example by using cyclones, centrifugation, screening, or any other suitable particulates removal or separation systems. As will be appreciated by one of skill in the art, and with the help of this disclosure, coke is an undesired by-product in the process for producing ethylene and benzene as disclosed herein, and as such, the lower the amount of produced coke, the better.

[0055] In an aspect, the process for producing ethylene and benzene as disclosed herein can be characterized by a selectivity to coke of less than about 25%, alternatively less than about 20%, or alternatively less than about 15%. Generally, a selectivity to a certain product (whether desired or undesired) refers to the amount of that particular product formed divided by the total amount of products formed.

[0056] In an aspect, the process for producing ethylene and benzene as disclosed herein can be characterized by a selectivity to ethylene and benzene of equal to or greater than about 50%, alternatively equal to or greater than about 60%, or alternatively equal to or greater than about 75%.

[0057] In an aspect, a process for producing ethylene and benzene as disclosed herein can comprise (a) introducing a fuel gas stream and an oxidant gas to a combustion zone to produce a combustion product; (b) introducing a first reactant mixture to a first reaction zone, wherein the first reactant mixture comprises a hydrocarbon stream and at least a portion of the combustion product, and wherein the combustion product heats the hydrocarbon stream to a first temperature effective for a pyrolysis reaction, wherein the first temperature is equal to or greater than about 2,000 °C; (c) allowing at least a portion of the first reactant mixture to react via the pyrolysis reaction and produce a pyrolysis reaction product, wherein the pyrolysis reaction product comprises unconverted hydrocarbons, acetylene (C_2H_2), ethylene (C_2H_4), carbon monoxide (CO), hydrogen (H_2), water (H_2O), and carbon dioxide (CO_2); (d) cooling at least a portion of the pyrolysis reaction product in a quench zone to form a cooled pyrolysis reaction product, wherein a first reactor comprises the combustion zone, the first reaction zone, and the quench zone; (e) introducing at least a portion of the cooled pyrolysis reaction product to a second reaction zone, wherein the cooled pyrolysis reaction product comprises (1) acetylene in an amount of from about 5 vol.% to about 30 vol.%, based on the total volume of the cooled pyrolysis reaction product, (2) hydrogen in an amount of from about 10 vol.% to about 70 vol.%, based on the total volume of the cooled pyrolysis reaction product, (3) methane in an amount of from about 5 vol.% to about 30

vol.%, based on the total volume of the cooled pyrolysis reaction product, and (4) carbon dioxide in an amount of from about 5 vol.% to about 30 vol.%, based on the total volume of the cooled pyrolysis reaction product; (f) allowing a first portion of the acetylene in the cooled pyrolysis reaction product to undergo hydrogenation to ethylene and a second portion of the acetylene in the cooled pyrolysis reaction product to undergo trimerization to benzene at a temperature of from about 850 °C to about 950 °C effective for acetylene hydrogenation to ethylene and/or acetylene trimerization to benzene (C_6H_6), to produce a second reaction zone effluent, wherein the second reaction zone effluent comprises unconverted hydrocarbons, unconverted C_2H_2 , C_2H_4 , C_6H_6 , CO, H_2 , H_2O , and CO_2 ; wherein an amount of C_2H_4 in the second reaction zone effluent is greater than an amount of C_2H_4 in the cooled pyrolysis reaction product; wherein a second reactor comprises the second reaction zone; wherein the second reactor comprises reactor lined with glass, quartz, ceramic, and the like, or combinations thereof; and wherein the second reaction zone comprises thermally conductive material particles, wherein the thermally conductive material particles are non-metallic and/or have non-metallic surfaces, and wherein coke is deposited on the thermally conductive material particles during step (f) to produce spent thermally conductive material particles; (g) separating at least a portion of the second reaction zone effluent into an ethylene stream, a benzene stream, a first CO_2 stream, a first syngas stream, and coke, wherein the first syngas stream comprises H_2 and CO; (h) regenerating at least a portion of the spent thermally conductive material particles to produce the thermally conductive material particles and a second CO_2 stream; (i) contacting at least a portion of the first CO_2 stream and/or at least a portion of the second CO_2 stream with hydrogen to produce a second syngas stream comprising H_2 and CO; and (j) introducing at least a portion of the first syngas stream and/or at least a portion of the second syngas stream a third reaction zone comprising a catalyst to produce a methanol stream. In such aspect, the process for producing ethylene and benzene as disclosed herein can be characterized by a selectivity to coke of less than about 15%, and by a selectivity to ethylene and benzene of equal to or greater than about 75%.

[0058] In an aspect, a process for producing ethylene and benzene as disclosed herein can advantageously display improvements in one or more process characteristics when compared to an otherwise similar process that does not integrate hydrocarbon pyrolysis with other processes for producing desired products. A synthesis gas (e.g., H_2 and CO) to methanol conversion process as disclosed herein can increase further the overall efficiency of the process by producing methanol

from the H₂ and CO obtained from hydrocarbon pyrolysis, as well as CO₂ hydrogenation. Methane catalytic conversion to benzene generally displays a very low conversion, and it is hindered by a high rate of catalyst deactivation. As such, thermal conversion of methane to acetylene, with subsequent thermal conversion of acetylene to both benzene and ethylene advantageously improves the overall process efficiency for the conversion of natural gas to aromatic hydrocarbons such as benzene. A further increase in overall process efficiency can be achieved by methanol production from the syngas produced in the process. The methanol can be advantageously used as a liquid fuel, and can be easily transported, as compared to transporting gases. Additional advantages of the process for producing ethylene and benzene as disclosed herein can be apparent to one of skill in the art viewing this disclosure.

EXAMPLES

[0059] The subject matter having been generally described, the following examples are given as particular embodiments of the disclosure and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification of the claims to follow in any manner.

EXAMPLE 1

[0060] The combustion and pyrolysis of methane was investigated at high temperature, and the products after pyrolysis were quenched to room temperature. The combustion and pyrolysis was conducted via three steps: (i) the combustion of fuel gases in a combustion chamber; (ii) mixing of cracking feed (natural gas/field gas) with the products of combustion in a mixing section; followed by (iii) the cracking or pyrolysis of the above mixture from step (ii) in the reactor section. The combustion chamber produced hot gases with a temperature of about 2,500 °C. The hot gases produced in the combustion chamber were mixed with feed natural gas which was optionally preheated to 300-500 °C. The combustion gases transferred heat to the feed natural gas by direct contact and the feed underwent pyrolysis. Major products from pyrolysis included acetylene (C₂H₂), ethylene (C₂H₄), and hydrogen (H₂). However carbon monoxide (CO), carbon dioxide (CO₂), and water were also formed, mostly from the combustion chamber. The products were quenched by water spray to <300 °C.

[0061] A sample from the quenched products was injected into a gas chromatograph (GC), which analyzed the composition of the quenched products. The results of the GC runs are displayed in Table 1.

Table 1

Natural gas for cracking		Run1	Run2	Run3	Run4
Natural Gas for Cracking	lb/h	43.5	43.6	48.0	48.7
Duty	MBtu/h	1114	1114	1113	1108
Natural Gas Fuel	lb/h	55.6	55.5	55.7	55.3
Oxygen	lb/h	182.8	182.0	180.1	177.7
O2 Stoichiometry	%	88.4%	88.0%	87.2%	86.5%
Cracked Gas composition on a water free basis					
H2	mol%	35.30	30.90	33.59	33.44
CO2	mol%	19.64	20.39	19.67	19.19
CH4	mol%	14.46	13.27	17.23	18.88
C2H4	mol%	0.48	1.58	0.55	0.63
C2H2	mol%	4.58	5.87	4.36	4.09
CO	mol%	24.09	25.76	22.85	21.90
Performance metrics of the cracker					
Conversion	% C	51.3%	59.1%	45.8%	41.5%
Cracking (C2 Yield)	% C	34.0%	45.6%	30.7%	29.2%
Acetylene Yield	% C	30.7%	35.9%	27.3%	25.3%

[0062] The data in Table 1 provides a typical composition of various gas streams produced in the methane combustion and pyrolysis as disclosed herein. As can be seen from data in Table 1, a C₂ yield of about 30% was achieved. The achieved C₂ yield is high by comparison with the maximum C₂ yield (less than 24%, as outlined in J. Chem. Soc., Chem. Commun., 1992, p. 1546, which is incorporated by reference herein in its entirety) that can be obtained via catalytic oxidative methane coupling.

EXAMPLE 2

[0063] The thermal conversion of acetylene to ethylene and benzene in the presence of carbon dioxide was investigated. Acetylene, present in a mixture of gases C₂H₂ + H₂ + CO₂, was subjected to hydrogenation and trimerization in an empty quartz reactor with a 4 mm internal diameter (I.D.) and with a length of 15 cm, at a temperature of 915°C, and at a total flow rate of 50 cc/min, as illustrated in Figure 2. The reactor was located inside of an electrically heated furnace. The outlet gases comprised unconverted C₂H₂, C₂H₄, C₆H₆, CH₄, CO, H₂, CO₂, and coke. The conversion of acetylene was 92%, with a total selectivity to C₂H₄ + benzene of 69%. For purposes of the disclosure herein, the conversion of a reagent is a % conversion based on moles converted. CO selectivity was 23%, and coke selectivity was 8%.

EXAMPLE 3

[0064] The thermal conversion of acetylene to ethylene and benzene in the presence of carbon dioxide was investigated. Acetylene, present in a mixture of gases $C_2H_2 + H_2 + CO_2$, was subjected to hydrogenation and trimerization in a quartz reactor having a 4 mm I.D. and a length of 15 cm, filled with quartz particles (thermally conductive material particles) at a temperature of 915°C, and at a total flow rate of 50 cc/min, as illustrated in Figure 3. The reactor was located inside of an electrically heated furnace. The outlet gases comprised C_2H_4 , C_6H_6 , CH_4 , CO , H_2 , CO_2 , and coke. The conversion of acetylene was 98%, with a total selectivity to $C_2H_4 +$ benzene of 63%. CO selectivity was 22%, and coke selectivity was 15%.

EXAMPLE 4

[0065] The thermal conversion of acetylene to ethylene and benzene in the presence of carbon dioxide was investigated. Acetylene, present in a mixture of gases $C_2H_2 + H_2 + CO_2$, was subjected to hydrogenation and trimerization in a quartz reactor having a 4 mm I.D. and a length of 15 cm, filled with a zeolite catalyst (ZSM-5) at a temperature of 915°C, and at a total flow rate of 40 cc/min, as illustrated in Figure 4. The reactor was located inside of an electrically heated furnace. The outlet gases comprised C_2H_4 , C_6H_6 , CH_4 , CO , H_2 , CO_2 , and coke. The conversion of acetylene was 100%, with a total selectivity to $C_2H_4 +$ benzene of 27%. CO selectivity was 7%, and coke selectivity was 66%.

EXAMPLE 5

[0066] The thermal conversion of acetylene to ethylene and benzene in the presence of carbon dioxide was investigated. Acetylene, present in a mixture of gases $C_2H_2 + H_2 + CO_2$, was subjected to hydrogenation and trimerization in a quartz reactor having a 4 mm I.D. and a length of 15 cm, filled with quartz sand as a thermo-contact material (thermally conductive material particles), and having an outer regeneration zone, as illustrated in Figure 5. The contact material can carry the heat, accumulated from regeneration zone, to the reaction zone for the endothermic conversion of acetylene to mixture of hydrocarbons (comprising ethylene and benzene). The regeneration process comprised burning off coke fragments accumulated on contact material to produce heat. Temperatures in the reaction and regeneration zone were 900°C - 915°C. The outlet gases comprised C_2H_4 , C_6H_6 , CH_4 , CO , H_2 , CO_2 , and coke. The conversion of acetylene was 96%, with a total selectivity to $C_2H_4 +$ benzene of 65%. CO selectivity was 18%, and coke selectivity was 17%. Further, CO_2 separated from a regeneration gas could be connected with a

main stream CO/CO₂ stream of a reactor outlet and could be converted to syngas, and subsequently to methanol.

[0067] For the purpose of any U.S. national stage filing from this application, all publications and patents mentioned in this disclosure are incorporated herein by reference in their entireties, for the purpose of describing and disclosing the constructs and methodologies described in those publications, which might be used in connection with the methods of this disclosure. Any publications and patents discussed herein are provided solely for their disclosure prior to the filing date of the present application. Nothing herein is to be construed as an admission that the inventors are not entitled to antedate such disclosure by virtue of prior invention.

[0068] In any application before the United States Patent and Trademark Office, the Abstract of this application is provided for the purpose of satisfying the requirements of 37 C.F.R. § 1.72 and the purpose stated in 37 C.F.R. § 1.72(b) “to enable the United States Patent and Trademark Office and the public generally to determine quickly from a cursory inspection the nature and gist of the technical disclosure.” Therefore, the Abstract of this application is not intended to be used to construe the scope of the claims or to limit the scope of the subject matter that is disclosed herein. Moreover, any headings that can be employed herein are also not intended to be used to construe the scope of the claims or to limit the scope of the subject matter that is disclosed herein. Any use of the past tense to describe an example otherwise indicated as constructive or prophetic is not intended to reflect that the constructive or prophetic example has actually been carried out.

[0069] The present disclosure is further illustrated by the following examples, which are not to be construed in any way as imposing limitations upon the scope thereof. On the contrary, it is to be clearly understood that resort can be had to various other aspects, embodiments, modifications, and equivalents thereof which, after reading the description herein, can be suggest to one of ordinary skill in the art without departing from the spirit of the present invention or the scope of the appended claims.

ADDITIONAL DISCLOSURE

[0070] A first aspect, which is a process for ethylene and benzene comprising (a) introducing a fuel gas stream and an oxidant gas to a combustion zone to produce a combustion product; (b) introducing a first reactant mixture to a first reaction zone, wherein the first reactant mixture comprises a hydrocarbon stream and at least a portion of the combustion product, and wherein

the combustion product heats the hydrocarbon stream to a first temperature effective for a pyrolysis reaction; (c) allowing at least a portion of the first reactant mixture to react via the pyrolysis reaction and produce a pyrolysis reaction product, wherein the pyrolysis reaction product comprises unconverted hydrocarbons, acetylene (C_2H_2), ethylene (C_2H_4), carbon monoxide (CO), hydrogen (H_2), water (H_2O), and carbon dioxide (CO_2); (d) cooling at least a portion of the pyrolysis reaction product in a quench zone to form a cooled pyrolysis reaction product, wherein the cooled pyrolysis reaction product is characterized by a second temperature, and wherein the second temperature is lower than the first temperature; (e) introducing the cooled pyrolysis reaction product to a second reaction zone; (f) allowing a first portion of the acetylene in the cooled pyrolysis reaction product to undergo hydrogenation to ethylene and a second portion of the acetylene in the cooled pyrolysis reaction product to undergo trimerization to benzene, to produce a second reaction zone effluent, wherein the second reaction zone effluent comprises unconverted hydrocarbons, unconverted C_2H_2 , C_2H_4 , benzene (C_6H_6), CO, H_2 , H_2O , and CO_2 ; and wherein an amount of C_2H_4 in the second reaction zone effluent is greater than an amount of C_2H_4 in the cooled pyrolysis reaction product; and (g) separating at least a portion of the second reaction zone effluent into an ethylene stream, a benzene stream, a first CO_2 stream, and a first syngas stream, wherein the first syngas stream comprises H_2 and CO.

[0071] A second aspect, which is the process of the first aspect, wherein the second reaction zone is contained within a glass-lined reactor, a quartz-lined reactor, or a ceramic-lined reactor.

[0072] A third aspect, which is the process of the second aspect, wherein the first reaction zone and the second reaction zone exclude a catalyst.

[0073] A fourth aspect, which is the process of the third aspect, wherein a common reactor comprises both the first reaction zone and the second reaction zone.

[0074] A fifth aspect, which is the process of the fourth aspect, wherein the common reactor has an inner common reactor surface, wherein at least a portion of the inner common reactor surface contacts the cooled pyrolysis reaction product, and wherein at least a portion of the inner common reactor surface is non-metallic.

[0075] A sixth aspect, which is the process of the fifth aspect, wherein the inner common reactor surface comprises glass, quartz, ceramic, or combinations thereof.

[0076] A seventh aspect, which is the process of any one of the first through the sixth aspects, wherein at least a portion of the common reactor is lined with glass, quartz, ceramic, or combinations thereof.

[0077] An eighth aspect, which is the process of any one of the first through the seventh aspects, wherein the common reactor further comprises the quench zone and optionally the combustion zone.

[0078] A ninth aspect, which is the process of any one of the first through the eighth aspects, wherein the common reactor comprises an autothermal reactor.

[0079] A tenth aspect, which is the process of the third aspect, wherein a first reactor comprises the first reaction zone, and wherein a second reactor comprises the second reaction zone.

[0080] An eleventh aspect, which is the process of the tenth aspect, wherein the second reactor has an inner second reactor surface, wherein at least a portion of the inner second reactor surface contacts the cooled pyrolysis reaction product.

[0081] A twelfth aspect, which is the process of the eleventh aspect, wherein the inner second reactor surface is non-metallic.

[0082] A thirteenth aspect, which is the process of any one of the tenth through the twelfth aspects, wherein the inner second reactor surface comprises glass, quartz, ceramic, or combinations thereof.

[0083] A fourteenth aspect, which is the process of any one of the tenth through the thirteenth aspects, wherein the first reactor further comprises the quench zone.

[0084] A fifteenth aspect, which is the process of the fourteenth aspect, wherein the first reactor further comprises the combustion zone.

[0085] A sixteenth aspect, which is the process of any one of the first through the fifteenth aspects, wherein the second reaction zone excludes liquid phase hydrogenation of acetylene to ethylene.

[0086] A seventeenth aspect, which is the process of any one of the first through the sixteenth aspects, wherein the first temperature is equal to or greater than about 2,000 °C.

[0087] An eighteenth aspect, which is the process of any one of the first through the seventeenth aspects, wherein the second temperature is a temperature effective for acetylene hydrogenation to ethylene and/or acetylene trimerization to C₆H₆.

[0088] A nineteenth aspect, which is the process of any one of the first through the eighteenth aspects, wherein the second temperature is from about 600 °C to about 1,000 °C.

[0089] A twentieth aspect, which is the process of any one of the first through the nineteenth aspects, wherein the second temperature is from about 850 °C to about 950 °C.

[0090] A twenty-first aspect, which is the process of any one of the first through the twentieth aspects, wherein the second reaction zone comprises thermally conductive material particles.

[0091] A twenty-second aspect, which is the process of the twenty-first aspect, wherein the thermally conductive material particles are non-metallic and/or have non-metallic surfaces.

[0092] A twenty-third aspect, which is the process of any one of the first through the twenty-second aspects, wherein the thermally conductive material particles comprise glass, quartz, ceramic, or combinations thereof.

[0093] A twenty-fourth aspect, which is the process of any one of the first through the twenty-third aspects, wherein coke is deposited on the thermally conductive material particles during step (f) to produce spent thermally conductive material particles, and wherein at least a portion of the spent thermally conductive material particles is regenerated to produce the thermally conductive material particles and a second CO₂ stream.

[0094] A twenty-fifth aspect, which is the process of the twenty-fourth aspect, wherein at least a portion of the first CO₂ stream and/or at least a portion of the second CO₂ stream is contacted with hydrogen to produce a second syngas stream comprising H₂ and CO.

[0095] A twenty-sixth aspect, which is the process of the twenty-fifth aspect, wherein the second syngas stream is characterized by a H₂/CO molar ratio of from about 1:1 to about 2:1.

[0096] A twenty-seventh aspect, which is the process of any one of the first through the twenty-sixth aspects, wherein at least a portion of the first syngas stream and/or at least a portion of the second syngas stream is introduced to a third reaction zone comprising a catalyst to produce a methanol stream.

[0097] A twenty-eighth aspect, which is the process of the twenty-seventh aspect, wherein the catalyst for the third reaction zone comprises Cu, Cu/ZnO, Cu/ThO₂, Cu/Zn/Al₂O₃, Cu/ZnO/Al₂O₃, Cu/Zr, or combinations thereof.

[0098] A twenty-ninth aspect, which is the process of any one of the first through the twenty-eighth aspects, wherein the first syngas stream is characterized by a H₂/CO molar ratio of from about 1:1 to about 2:1.

[0099] A thirtieth aspect, which is the process of any one of the first through the twenty-ninth aspects, wherein the first CO₂ stream is separated from the second reaction zone effluent by amine absorption.

[00100] A thirty-first aspect, which is the process of any one of the first through the thirtieth aspects, wherein the fuel gas stream and the hydrocarbon stream are the same or different.

[00101] A thirty-second aspect, which is the process of any one of the first through the thirty-first aspects, wherein the fuel gas stream and/or the hydrocarbon stream comprise methane, ethane, propane, natural gas, natural gas liquids, associated gas, well head gas, enriched gas, heavy hydrocarbons, petcoke, naphtha, heavy oil, heavy oil residue, or combinations thereof.

[00102] A thirty-third aspect, which is the process of any one of the first through the thirty-second aspects, wherein the oxidant gas comprises oxygen, purified oxygen, air, oxygen-enriched air, or combinations thereof.

[00103] A thirty-fourth aspect, which is the process of any one of the first through the thirty-third aspects, wherein coke is further separated from the second reaction zone effluent.

[00104] A thirty-fifth aspect, which is the process of the thirty-fourth aspect, wherein a selectivity to coke is less than about 25%.

[00105] A thirty-sixth aspect, which is the process of any one of the first through the thirty-fifth aspects, wherein a selectivity to ethylene and benzene is equal to or greater than about 50%.

[00106] A thirty-seventh aspect, which is a process for producing ethylene and benzene comprising (a) introducing a fuel gas stream and an oxidant gas to a combustion zone to produce a combustion product; (b) introducing a first reactant mixture to a first reaction zone, wherein the first reactant mixture comprises a hydrocarbon stream and at least a portion of the combustion product, and wherein the combustion product heats the hydrocarbon stream to a first temperature effective for a pyrolysis reaction, wherein the first temperature is equal to or greater than about 2,000 °C; (c) allowing at least a portion of the first reactant mixture to react via the pyrolysis reaction and produce a pyrolysis reaction product, wherein the pyrolysis reaction product comprises unconverted hydrocarbons, acetylene (C₂H₂), ethylene (C₂H₄), carbon monoxide (CO), hydrogen (H₂), water (H₂O), and carbon dioxide (CO₂); (d) cooling at least a portion of the

pyrolysis reaction product in a quench zone to form a cooled pyrolysis reaction product, wherein a first reactor comprises the combustion zone, the first reaction zone, and the quench zone; (e) introducing the cooled pyrolysis reaction product to a second reaction zone; (f) allowing a first portion of the acetylene in the cooled pyrolysis reaction product to undergo hydrogenation to ethylene and a second portion of the acetylene in the cooled pyrolysis reaction product to undergo trimerization to benzene at a temperature of from about 850 °C to about 950 °C effective for acetylene hydrogenation to ethylene and/or acetylene trimerization to benzene (C₆H₆), to produce a second reaction zone effluent, wherein the second reaction zone effluent comprises unconverted hydrocarbons, unconverted C₂H₂, C₂H₄, C₆H₆, CO, H₂, H₂O, and CO₂; wherein an amount of C₂H₄ in the second reaction zone effluent is greater than an amount of C₂H₄ in the cooled pyrolysis reaction product; wherein a second reactor comprises the second reaction zone; wherein the second reactor comprises a glass lined reactor, a quartz lined reactor, a ceramic lined reactor, or combinations thereof; and wherein the second reaction zone comprises thermally conductive material particles, wherein the thermally conductive material particles are non-metallic and/or have non-metallic surfaces, and wherein coke is deposited on the thermally conductive material particles during step (f) to produce spent thermally conductive material particles; (g) separating at least a portion of the second reaction zone effluent into an ethylene stream, a benzene stream, a first CO₂ stream, a first syngas stream, and coke, wherein the first syngas stream comprises H₂ and CO; (h) regenerating at least a portion of the spent thermally conductive material particles to produce the thermally conductive material particles and a second CO₂ stream; (i) contacting at least a portion of the first CO₂ stream and/or at least a portion of the second CO₂ stream with hydrogen to produce a second syngas stream comprising H₂ and CO; and (j) introducing at least a portion of the first syngas stream and/or at least a portion of the second syngas stream a third reaction zone comprising a catalyst to produce a methanol stream.

[00107] A thirty-eighth aspect, which is the process of the thirty-seventh aspect, wherein a selectivity to coke is less than about 20%, and wherein a selectivity to ethylene and benzene is equal to or greater than about 60%.

[00108] While embodiments of the disclosure have been shown and described, modifications thereof can be made without departing from the spirit and teachings of the invention. The embodiments and examples described herein are exemplary only, and are not intended to be

limiting. Many variations and modifications of the invention disclosed herein are possible and are within the scope of the invention.

[00109] Accordingly, the scope of protection is not limited by the description set out above but is only limited by the claims which follow, that scope including all equivalents of the subject matter of the claims. Each and every claim is incorporated into the specification as an embodiment of the present invention. Thus, the claims are a further description and are an addition to the detailed description of the present invention. The disclosures of all patents, patent applications, and publications cited herein are hereby incorporated by reference.

CLAIMS

What is claimed is:

1. A process for producing ethylene and benzene comprising:
 - (a) introducing a fuel gas stream and an oxidant gas to a combustion zone to produce a combustion product;
 - (b) introducing a first reactant mixture to a first reaction zone, wherein the first reactant mixture comprises a hydrocarbon stream and at least a portion of the combustion product, and wherein the combustion product heats the hydrocarbon stream to a first temperature effective for a pyrolysis reaction;
 - (c) allowing at least a portion of the first reactant mixture to react via the pyrolysis reaction and produce a pyrolysis reaction product, wherein the pyrolysis reaction product comprises unconverted hydrocarbons, acetylene (C_2H_2), ethylene (C_2H_4), carbon monoxide (CO), hydrogen (H_2), water (H_2O), and carbon dioxide (CO_2);
 - (d) cooling at least a portion of the pyrolysis reaction product in a quench zone to form a cooled pyrolysis reaction product, wherein the cooled pyrolysis reaction product is characterized by a second temperature, and wherein the second temperature is lower than the first temperature;
 - (e) introducing the cooled pyrolysis reaction product to a second reaction zone;
 - (f) allowing a first portion of the acetylene in the cooled pyrolysis reaction product to undergo hydrogenation to ethylene and a second portion of the acetylene in the cooled pyrolysis reaction product to undergo trimerization to benzene, to produce a second reaction zone effluent, wherein the second reaction zone effluent comprises unconverted hydrocarbons, unconverted C_2H_2 , C_2H_4 , benzene (C_6H_6), CO, H_2 , H_2O , and CO_2 ; and wherein an amount of C_2H_4 in the second reaction zone effluent is greater than an amount of C_2H_4 in the cooled pyrolysis reaction product; and
 - (g) separating at least a portion of the second reaction zone effluent into an ethylene stream, a benzene stream, a first CO_2 stream, and a first syngas stream, wherein the first syngas stream comprises H_2 and CO.
2. The process of claim 1, wherein the second reaction zone is contained within a glass-lined reactor, a quartz-lined reactor, or a ceramic-lined reactor.

3. The process of claim 2, wherein the first reaction zone and the second reaction zone exclude a catalyst.
4. The process of claim 3, wherein a common reactor comprises both the first reaction zone and the second reaction zone.
5. The process of any one of claims 1-4, wherein the common reactor further comprises the quench zone and optionally the combustion zone.
6. The process of claim 3, wherein a first reactor comprises the first reaction zone, and wherein a second reactor comprises the second reaction zone.
7. The process of claim 6, wherein the second reactor has an inner second reactor surface, wherein at least a portion of the inner second reactor surface contacts the cooled pyrolysis reaction product, and wherein the inner second reactor surface is non-metallic.
8. The process of claim 7, wherein the inner second reactor surface comprises glass, quartz, ceramic, or combinations thereof.
9. The process of any one of claims 6-8, wherein the first reactor further comprises the quench zone and/or the combustion zone.
10. The process of any one of claims 1-9, wherein the second reaction zone excludes liquid phase hydrogenation of acetylene to ethylene.
11. The process of any one of claims 1-10, wherein the first temperature is equal to or greater than about 2,000 °C.
12. The process of any one of claims 1-11, wherein the second temperature is from about 600 °C to about 1,000 °C.
13. The process of any one of claims 1-12, wherein the second reaction zone comprises thermally conductive material particles, wherein the thermally conductive material particles are non-metallic and/or have non-metallic surfaces.
14. The process of claim 13, wherein the thermally conductive material particles comprise glass, quartz, ceramic, or combinations thereof.
15. The process of any one of claims 1-14, wherein coke is deposited on the thermally conductive material particles during step (f) to produce spent thermally conductive material particles, and wherein at least a portion of the spent thermally conductive material particles is regenerated to produce the thermally conductive material particles and a second CO₂ stream.

16. The process of claim 15, wherein at least a portion of the first CO₂ stream and/or at least a portion of the second CO₂ stream is contacted with hydrogen to produce a second syngas stream comprising H₂ and CO.
17. The process of any one of claims 1-16, wherein at least a portion of the first syngas stream and/or at least a portion of the second syngas stream is introduced to a third reaction zone comprising a catalyst to produce a methanol stream.
18. The process of any one of claims 1-17, wherein coke is further separated from the second reaction zone effluent, and wherein a selectivity to coke is less than about 25%.
19. The process of any one of claims 1-18, wherein a selectivity to ethylene and benzene is equal to or greater than about 50%.
20. A process for producing ethylene and benzene comprising:
- (a) introducing a fuel gas stream and an oxidant gas to a combustion zone to produce a combustion product;
 - (b) introducing a first reactant mixture to a first reaction zone, wherein the first reactant mixture comprises a hydrocarbon stream and at least a portion of the combustion product, and wherein the combustion product heats the hydrocarbon stream to a first temperature effective for a pyrolysis reaction, wherein the first temperature is equal to or greater than about 2,000 °C;
 - (c) allowing at least a portion of the first reactant mixture to react via the pyrolysis reaction and produce a pyrolysis reaction product, wherein the pyrolysis reaction product comprises unconverted hydrocarbons, acetylene (C₂H₂), ethylene (C₂H₄), carbon monoxide (CO), hydrogen (H₂), water (H₂O), and carbon dioxide (CO₂);
 - (d) cooling at least a portion of the pyrolysis reaction product in a quench zone to form a cooled pyrolysis reaction product, wherein a first reactor comprises the combustion zone, the first reaction zone, and the quench zone;
 - (e) introducing the cooled pyrolysis reaction product to a second reaction zone;
 - (f) allowing a first portion of the acetylene in the cooled pyrolysis reaction product to undergo hydrogenation to ethylene and a second portion of the acetylene in the cooled pyrolysis reaction product to undergo trimerization to benzene at a temperature of from about 850 °C to about 950 °C effective for acetylene hydrogenation to ethylene and/or acetylene trimerization to benzene (C₆H₆), to produce a second reaction zone effluent,

wherein the second reaction zone effluent comprises unconverted hydrocarbons, unconverted C_2H_2 , C_2H_4 , C_6H_6 , CO, H_2 , H_2O , and CO_2 ; wherein an amount of C_2H_4 in the second reaction zone effluent is greater than an amount of C_2H_4 in the cooled pyrolysis reaction product; wherein a second reactor comprises the second reaction zone; wherein the second reactor comprises a glass lined reactor, a quartz lined reactor, a ceramic lined reactor, or combinations thereof; and wherein the second reaction zone comprises thermally conductive material particles, wherein the thermally conductive material particles are non-metallic and/or have non-metallic surfaces, and wherein coke is deposited on the thermally conductive material particles during step (f) to produce spent thermally conductive material particles;

- (g) separating at least a portion of the second reaction zone effluent into an ethylene stream, a benzene stream, a first CO_2 stream, a first syngas stream, and coke, wherein the first syngas stream comprises H_2 and CO;
- (h) regenerating at least a portion of the spent thermally conductive material particles to produce the thermally conductive material particles and a second CO_2 stream;
- (i) contacting at least a portion of the first CO_2 stream and/or at least a portion of the second CO_2 stream with hydrogen to produce a second syngas stream comprising H_2 and CO; and
- (j) introducing at least a portion of the first syngas stream and/or at least a portion of the second syngas stream a third reaction zone comprising a catalyst to produce a methanol stream.

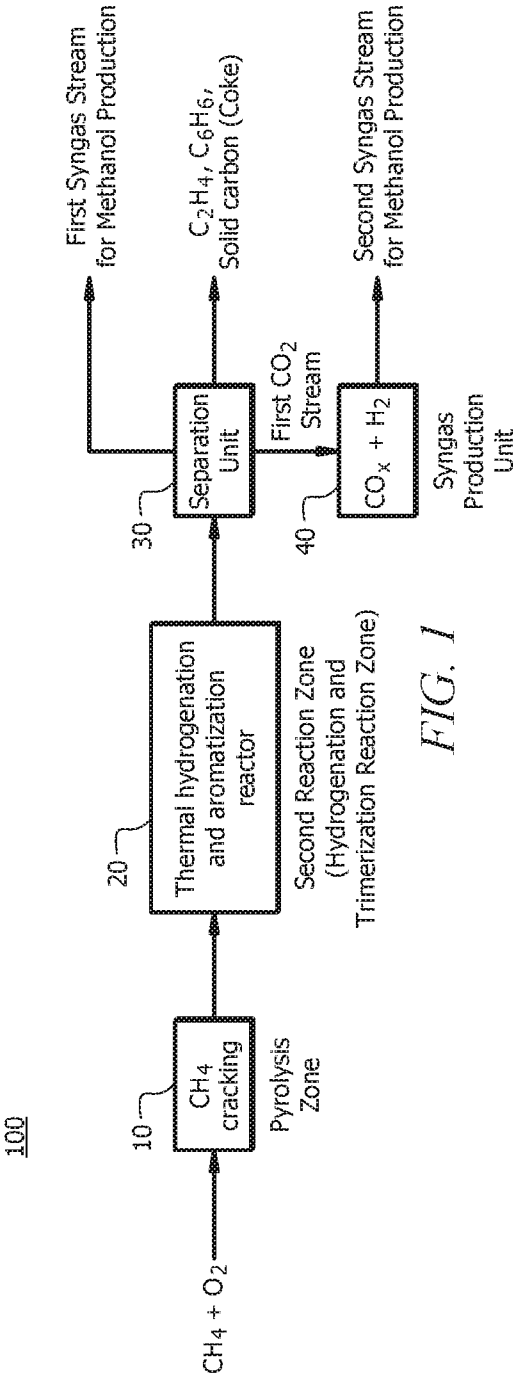
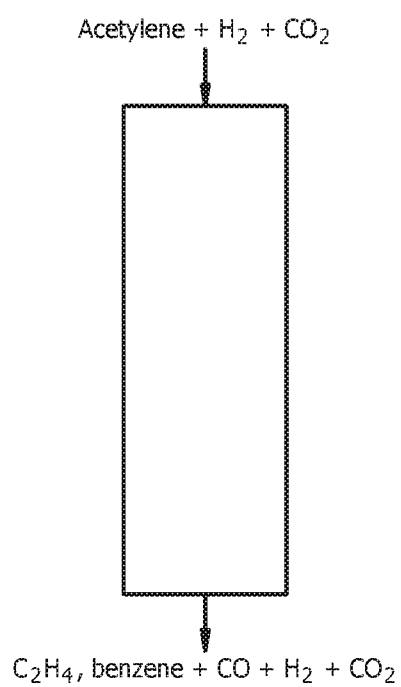
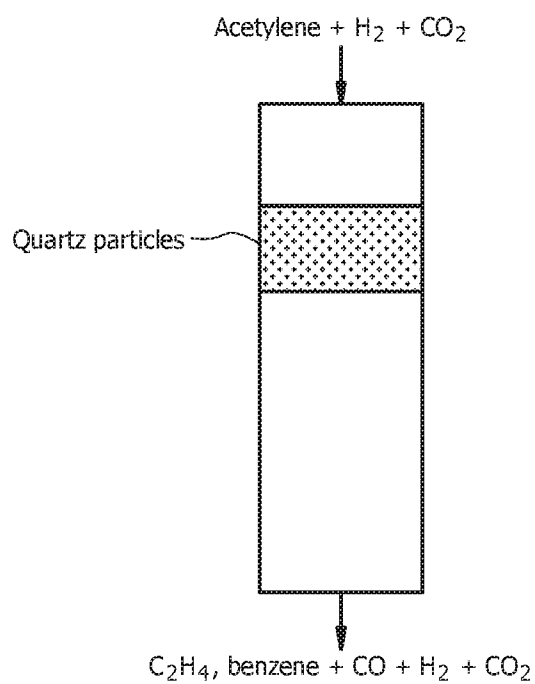


FIG. 1

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*FIG. 2**FIG. 3*

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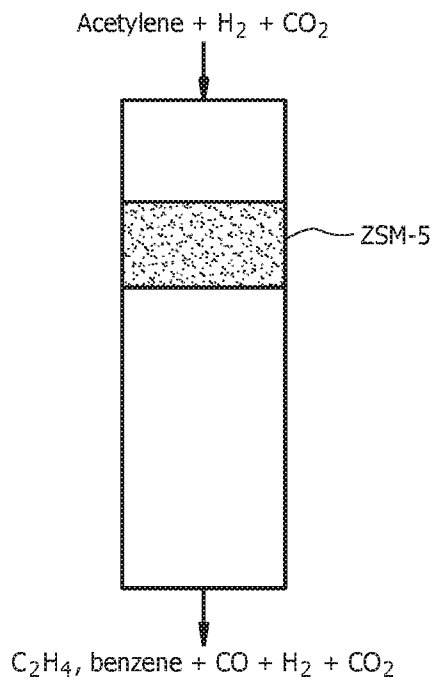


FIG. 4

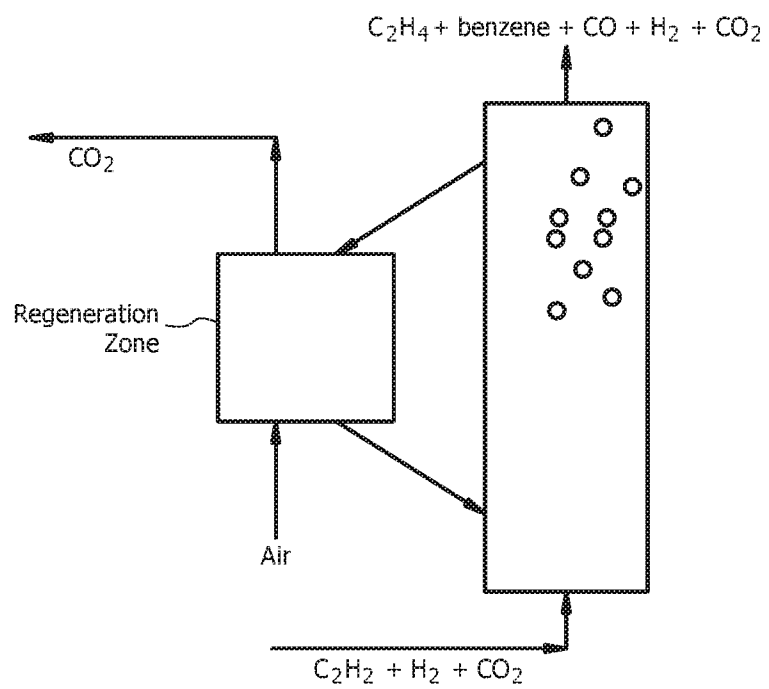


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2018/012064**A. CLASSIFICATION OF SUBJECT MATTER****C07C 5/09(2006.01)i, C07C 11/04(2006.01)i, C07C 2/48(2006.01)i, C07C 15/04(2006.01)i, C07C 11/24(2006.01)i**

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C 5/09; C07C 5/08; C07C 27/00; C07C 15/00; C07C 1/02; C07C 5/05; C07C 11/04; C07C 2/48; C07C 15/04; C07C 11/24

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: conversion, methane, ethylene, benzene, fuel gas, hydrocarbon, acetylene, hydrogenation, trimerization, pyrolysis

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 8080697 B2 (LIN, YUNGYI et al.) 20 December 2011 See abstract; column 4, lines 10-12; column 6, lines 42-52; column 8, lines 58-61; claims 1-16; and figures 1-10.	1-9
A		20
Y	US 8013198 B2 (MAMEDOV, AGADDIN et al.) 06 September 2011 See abstract; column 1, lines 44-55; column 2, lines 51-52; column 3, lines 1-5; and claim 1.	1-9
A	US 2009-0234167 A1 (RYU, J. YONG) 17 September 2009 See abstract; claims 1-24; and figures 1-2.	1-9, 20
A	US 6323247 B1 (HALL, KENNETH R. et al.) 27 November 2001 See abstract; claims 1-36; and figures 1-3.	1-9, 20
A	US 3156733 A (HAPPEL, JOHN et al.) 10 November 1964 See claims 1-6; and figures 1-4.	1-9, 20



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

30 April 2018 (30.04.2018)

Date of mailing of the international search report

30 April 2018 (30.04.2018)

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea



Facsimile No. +82-42-481-8578

Authorized officer

KAM, Yoo Lim

Telephone No. +82-42-481-3516



Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 14,16
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claims 14 and 16 do not comply with PCT Article 6 because they are referring to unsearchable claims 13 and 15 respectively.

3. ☒ Claims Nos.: 10-13,15,17-19
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2018/012064

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