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- (71) Applicant (for US only): **SHELL OIL COMPANY**
[US/US]; One Shell Plaza, P.O. Box 2463, Houston, Texas
77252-2463 (US).
- (71) Applicant (for all designated States except US): **SHELL
INTERNATIONALE RESEARCH MAATSCHAPPIJ
B.V.** [NL/NL]; Carel van Bylandtlaan 30, NL-2596 The
Hague (NL).
- (72) Inventors: **GEERLINGS, Jacobus Johannes Cornelis;**
Grasweg 31, 1031HW Amsterdam (NL). **MESTERS, Car-**

olus Matthias Anna Maria; 3923 Lakeridge Canyon
Drive, Sugar Land, Texas 77498 (US).

- (74) Agent: **GOSALIA, Sejal R.;** Shell Oil Company, One
Shell Plaza, P.O. Box 2463, Houston, Texas 77252-2463
(US).

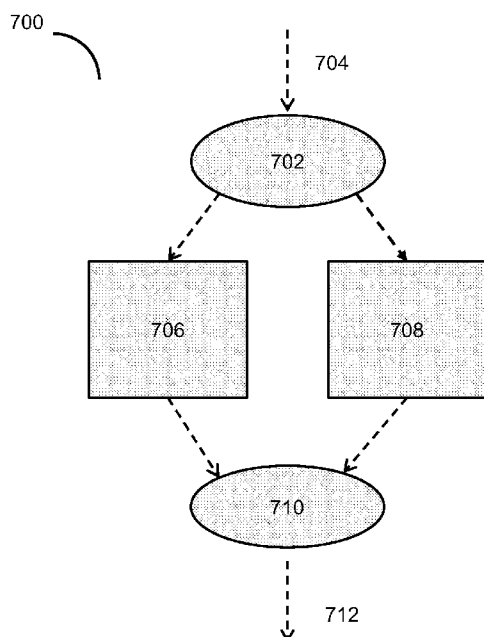
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- (54) Title: **PALLADIUM COATED METALS AS HYDROGEN ACCEPTORS FOR THE AROMATIZATION OF A METHANE
CONTAINING GAS STREAM**

Figure 7



(57) Abstract: Implementations of the disclosed subject matter provide a process for the aromatization of a methane-containing gas stream including contacting the methane-containing gas stream in a reaction zone of an aromatization reactor comprising an aromatization catalyst and a hydrogen acceptor under methane-containing gas aromatization conditions to produce reaction products comprising aromatics and gaseous hydrogen. At least a portion of the gaseous hydrogen produced is bound by the hydrogen acceptor in the reaction zone and removed from the reaction products and the reaction zone. The hydrogen acceptor includes a palladium barrier layer surrounding at least a portion of the outer surface of the hydrogen acceptor.



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PALLADIUM COATED METALS AS HYDROGEN ACCEPTORS FOR THE AROMATIZATION OF A METHANE CONTAINING GAS STREAM

CROSS-REFERENCE TO RELATED APPLICATIONS

5 [0001] This application claims priority to U.S. Provisional Application Serial No. 62/172,504 filed June 8, 2015, the entire disclosure of which is hereby incorporated by reference. This application is also related to co-pending U.S. Patent Application Ser. No. 14/395,819, entitled "AROMATIZATION OF A METHANE-CONTAINING GAS STREAM", which claims priority to U.S. Provisional Application No. 61/636,915 filed on 10 April 23, 2012, the disclosure of which is incorporated herein by reference. This application is also related to co-pending U.S. Patent Application Ser. No. 14/395,821, entitled "A PROCESS FOR THE AROMATIZATION OF A METHANE-CONTAINING GAS STREAM", which claims priority to U.S. Provisional Application No. 61/636,906 filed on April 23, 2012, the disclosure of which is incorporated herein by reference.

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TECHNICAL FIELD OF THE INVENTION

[0002] This disclosed subject matter relates to a process for the aromatization of a methane-containing gas stream to form aromatics and hydrogen in a reactor containing both catalyst and palladium coated hydrogen acceptor particles in a reactor wherein 20 removal of hydrogen from the reaction zone is accomplished *insitu* by the palladium-coated hydrogen acceptor, and wherein the palladium is a barrier that is selectively permeable for hydrogen only.

BACKGROUND

25 [0003] The aromatic hydrocarbons (specifically benzene, toluene and xylenes) are the main high-octane bearing components of the gasoline pool and important petrochemical building blocks used to produce high value chemicals and a variety of consumer products, for example, styrene, phenol, polymers, plastics, medicines, and others. Since the late 1930's, aromatics are primarily produced by upgrading of oil-derived feedstocks via 30 catalytic reforming or cracking of heavy naphthas. However, occasional severe oil shortages and oil price spikes result in severe aromatics shortages and aromatics price spikes. Therefore, there is a need to develop new, independent from oil, commercial routes to produce high value aromatics from highly abundant and inexpensive hydrocarbon

feedstocks such as methane or stranded natural gas (which typically contains about 80-90 % vol. methane).

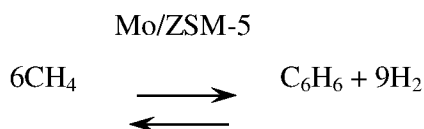
[0004] There are enormous proven reserves of stranded natural gas around the world. According to some estimates, the world reserves of natural gas are at least equal to those of oil. However, unlike the oil reserves that are primarily concentrated in a few oil-rich countries and are extensively utilized, upgraded and monetized, the natural gas reserves are much more broadly distributed around the world and significantly underutilized. Many developing countries that have significant natural gas reserves lack the proper infrastructure to exploit them and convert or upgrade them to higher value products. Quite often, in such situations, natural gas is flared to the atmosphere and wasted. Because of the above reasons, there is enormous economic incentive to develop new technologies that can efficiently convert methane or natural gas to higher value chemical products, specifically aromatics.

[0005] In 1993, Wang et al., (*Catal. Lett.* 1993, 21, 35-41), discovered a direct, non-oxidative route to partially convert methane to benzene by contacting methane with a catalyst containing 2.0 % wt. Molybdenum on an H-ZSM-5 zeolite support at atmospheric pressure and a temperature of 700 °C. Since Wang's discovery, numerous academic and industrial research groups have become active in this area and have contributed to further developing various aspects of the direct, non-oxidative methane to benzene catalyst and process technology. Many catalyst formulations have been prepared and tested and various reactor and process conditions and schemes have been explored.

[0006] Despite these efforts, a direct, non-oxidative methane aromatization catalyst and process cannot yet be commercialized. Some important challenges that need to be overcome to commercialize this process include: (i) the very low, as dictated by thermodynamic equilibrium, per pass conversion and benzene yield (for example, 10 % wt. and 6 % wt., respectively at 700 °C); (ii) the fact that the reaction is favored by high temperature and low pressure; (iii) the need to separate the produced aromatics and hydrogen from unreacted (mainly methane) hydrocarbon off gas and (iv) the rapid coke formation and deposition on the catalyst surface and corresponding relatively fast catalyst deactivation. Among these challenges, overcoming the thermodynamic equilibrium limitations and significantly improving (e.g., by greater than 3 times) the conversion and benzene yield per pass has the potential to enable the commercialization of an efficient,

direct, non-oxidative methane-containing gas aromatization process.

The methane aromatization reaction can be described as follows:



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[0007] According to the reaction, 6 molecules of methane are required to generate a molecule of benzene. It is also apparent that, the production of a molecule of benzene is accompanied by the production of 9 molecules of hydrogen. Simple thermodynamic calculations revealed and experimental data have confirmed that, the methane aromatization at atmospheric pressure is equilibrium limited to about 10 or 20 % wt. at reaction temperatures of 700 °C or 800 °C, respectively. In addition, experimental data showed that the above conversion levels correspond to about 6 and 11.5 % wt. benzene yield at 700 °C and 800 °C, respectively. The aforementioned low methane conversions and benzene yields per pass are not attractive and do not provide an economic justification for scale-up and commercialization of a methane containing gas aromatization process.

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[0008] Therefore, there is a need to develop an improved direct, non-oxidative methane aromatization process that provides for significantly higher (than those allowed by the thermodynamic equilibrium) methane conversion and benzene yields per pass by implementing an *insitu* hydrogen removal from the reaction products and the reaction zone.

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BRIEF SUMMARY

[0009] According to an embodiment of the disclosed subject matter, a process may include contacting the methane-containing gas stream in a reaction zone of an aromatization reactor comprising an aromatization catalyst and a hydrogen acceptor under methane-containing gas aromatization conditions to produce reaction products comprising aromatics and gaseous hydrogen. Further, at least a portion of the gaseous hydrogen produced is bound by the hydrogen acceptor in the reaction zone and removed from the reaction products and the reaction zone. The hydrogen acceptor comprises a palladium barrier layer surrounding at least a portion of the outer surface of the hydrogen acceptor.

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[0010] According to an implementation of the disclosed subject matter, novel processes and reactor schemes that employ single or multiple catalysts and/or hydrogen acceptor arrangements are provided.

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[0011] The disclosed subject matter also provides catalyst and/or hydrogen acceptor recycle and regeneration process schemes. According to these schemes, the catalyst and/or hydrogen acceptor are regenerated simultaneously or separately in single or in separate vessels and then returned to the reactor for continuous (uninterrupted) production of aromatics and hydrogen. The aforementioned insitu hydrogen removal in the reaction zone allows for overcoming the thermodynamic equilibrium limitations by introducing another chemical reaction, between gaseous hydrogen and the hydrogen acceptor. This results in significantly higher and economically more attractive methane-containing gas stream conversion and aromatics yields per pass relative to the process without hydrogen removal, i.e. without hydrogen acceptor in the reaction zone.

[0012] Additional features, advantages, and embodiments of the disclosed subject matter may be set forth or apparent from consideration of the following detailed description, drawings, and claims. Moreover, it is to be understood that both the foregoing summary and the following detailed description are examples and are intended to provide further explanation without limiting the scope of the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The accompanying drawings, which are included to provide a further understanding of the disclosed subject matter, are incorporated in and constitute a part of this specification. The drawings also illustrate embodiments of the disclosed subject matter and together with the detailed description serve to explain the principles of embodiments of the disclosed subject matter. No attempt is made to show structural details in more detail than may be necessary for a fundamental understanding of the disclosed subject matter and various ways in which it may be practiced.

[0014] FIG. 1 shows an example aromatization reactor with catalyst and palladium coated hydrogen acceptor particles intermixed in a fluidized bed according to an embodiment of the disclosed subject matter.

[0015] FIG. 2 shows an example fixed-bed aromatization reactor with catalyst and hydrogen acceptor particles in a fixed bed configuration according to an implementation of the disclosed subject matter.

[0016] FIG. 3 shows an example hydrogen acceptor including a palladium barrier layer according to an embodiment of the disclosed subject matter.

[0017] FIG. 4 shows an example single particle combining an aromatization catalyst with a palladium-coated hydrogen acceptor according to an embodiment of the disclosed subject matter.

[0018] FIG. 5 shows an example a palladium-coated hydrogen acceptor having a porous net-shaped structure according to an embodiment of the disclosed subject matter.

[0019] FIG. 6 shows a schematic diagram of a regeneration of the intermixed catalyst and hydrogen acceptor particles in a single regeneration vessel according to an embodiment of the disclosed subject matter.

[0020] FIG. 7 shows a schematic diagram of separation and regeneration of catalyst and hydrogen acceptor particles in separate vessels according to an embodiment of the disclosed subject matter.

DETAILED DESCRIPTION

[0021] The conversion of a methane-containing gas stream to aromatics is typically carried out in an aromatization reactor comprising a catalyst, which is active in the conversion of the methane-containing gas stream to aromatics. The methane-containing gas stream that is fed to the reactor comprises more than 50 % vol. methane, more than 60 % vol. methane, more than 70 % vol. methane and from 75 % vol. to 100 % vol. methane. The balance of the methane-containing gas may be other alkanes, for example, ethane, propane and butane. The methane-containing gas stream may be natural gas which is a naturally occurring hydrocarbon gas mixture consisting primarily of methane, with up to about 30 % vol. concentration of other hydrocarbons (usually mainly ethane and propane) as well as small amounts of other impurities such as carbon dioxide, nitrogen and others. The methane-containing gas stream may also include recycled unconverted methane which may include products from the aromatization reactions like hydrogen, benzene and naphthalene due to incomplete separation.

[0022] Various methane aromatization conditions may be set for carrying out the conversion of the methane-containing gas stream. In general, the conversion of a methane-containing gas stream is carried out at a gas hourly space velocity of from 100 to 60000 h⁻¹, a pressure of from 1 to 100 barg and a temperature of from 500 to 900 °C. In an embodiment, the conversion is carried out at gas hourly space velocity of from 300 to 30000 h⁻¹, a pressure of from 3 to 50 barg and a temperature of from 600 to 875 °C. In

another embodiment, the conversion is carried out at gas hourly space velocity of from 500 to 10000 h⁻¹, a pressure of from 5 to 25 barg and a temperature of from 650 to 850 °C.

[0023] Various co-feeds such as CO, CO₂ or hydrogen or mixtures thereof that react with coke precursors or prevent their formation during methane aromatization could be added at levels of < 10 % vol. to the methane-containing feed to improve the stability, performance or regenerability of the catalyst. The methane-containing gas aromatization is then carried out until conversion falls to values that are lower than those that are economically acceptable. At this point, the aromatization catalyst has to be regenerated to restore its aromatization activity to a level similar to its original activity. Following the regeneration, the catalyst is again contacted with a methane-containing gas stream in the reaction zone of the aromatization reactor under aromatization conditions for continuous production of aromatics.

[0024] The aromatization reaction of the disclosed subject matter is carried out in an aromatization reactor. To enable this, a suitably shaped and sufficiently robust catalyst and hydrogen acceptor are used for the reaction. A significant advantage of the process of the disclosed subject matter is that it provides for *insitu* removal of produced hydrogen from the reaction products and reaction zone. As a result, the disclosed subject matter results in a significant increase of both methane-containing gas stream conversion and benzene yield per pass to values that are significantly higher relative to these dictated by the methane aromatization reaction equilibrium. This is enabled by mixing and/or placing the catalyst and hydrogen acceptor particles in a fluidized-bed state in the reaction zone or the aromatization reactor (e.g., see Figure 1). For example, as shown in Figure 1, a fluidized bed reactor 10 comprises a mixture of catalyst and hydrogen acceptor particles in the fluidized bed 18. The methane-containing gas stream, the catalyst and hydrogen acceptors are introduced via one or more inlets 20 and the products, unreacted gases, catalyst and hydrogen acceptor are removed from the bed via one or more outlets 12. The feed and products flow upward in the direction of arrow 16. The catalyst and hydrogen acceptor are introduced upwardly in the direction of arrow 14 (although the catalyst and hydrogen acceptor then form a fluidized bed).

[0025] According to an implementation, Figure 2 shows a fixed-bed aromatization reactor with catalyst and hydrogen acceptor particles intermixed in a fixed bed configuration. As shown, a reactor 100 with a fixed bed 105 may include a mixture 130 of separate catalyst and hydrogen acceptor particles or single composite particles comprising

both the catalyst and hydrogen acceptor (as shown, and discussed below referring to Fig. 4). The process gas flows downward into the fixed bed 105 through gas inlet 140 and outward from the fixed bed 105 through gas outlet 150, as shown by the arrows 140, 150.

[0026] Any catalyst suitable for methane-containing gas stream aromatization may be used in the process of the disclosed subject matter. The catalyst typically comprises one or more active metals deposited on an inorganic oxide support and may optionally comprise promoters or other beneficial compounds. The active metal or metals, promoters, compounds as well as the inorganic support all contribute to the overall aromatization activity, mechanical strength and performance of the aromatization catalyst.

[0027] The active metal(s) component of the catalyst may be any metal that exhibits catalytic activity when contacted with a gas stream comprising methane under methane-containing gas aromatization conditions. The active metal may be selected from the group consisting of: vanadium, chromium, manganese, zinc, iron, cobalt, nickel, copper, gallium, germanium, niobium, molybdenum, ruthenium, rhodium, silver, tantalum, tungsten, rhenium, platinum and lead and mixtures thereof. The active metal is preferably molybdenum.

[0028] The promoter or promoters may be any element or elements that, when added in a certain preferred amount and by a certain preferred method of addition during catalyst synthesis, improve the performance of the catalyst in the methane-containing gas stream aromatization reaction.

[0029] The inorganic oxide support can be any support that, when combined with the active metal or metals and optionally the promoter or promoters contributes to the overall catalyst performance exhibited in the methane aromatization reaction. The support has to be suitable for treating or impregnating with the active metal compound or solution thereof and a promoter compound or solution thereof. The inorganic support preferably has a well-developed porous structure with sufficiently high surface area and pore volume and suitable for aromatization surface acidity. The inorganic oxide support may be one or more of zeolites, non-zeolitic molecular sieves, silica, alumina, zirconia, titania, yttria, ceria, rare earth metal oxides and mixtures thereof. The inorganic oxide support of the disclosed subject matter contains zeolite as the primary component. The zeolite may be a ZSM-5, ZSM-22, ZSM-8, ZSM-11, ZSM-12 or ZSM-35 zeolite structure types. The zeolite is preferably a ZSM-5 zeolite. The ZSM-5 zeolite further may have a SiO₂/Al₂O₃ ratio of 10 to 100 mass/mass. Preferably, the SiO₂/Al₂O₃ ratio of the zeolite is in the range of 20-50.

Even more preferably the SiO₂/Al₂O₃ ratio is from 20 to 40 and most preferably about 30. The support may optionally contain about 15-70% wt of a binder that binds the zeolite powder particles together and allows for shaping of the catalyst in the desired form and for achieving the desired high catalyst mechanical strength necessary for operation in a commercial aromatization reactor. More preferably the support contains from 15-30 % wt. binder. The binder is selected from the group consisting of silica, alumina, zirconia, titania, yttria, ceria, rare earth oxides or mixtures thereof.

[0030] The aromatization catalyst could be a monolithic structure, a porous net-shaped structure, a particle(s) in the form of cylindrical pellets, rings, spheres, and the like. As an example, in a fluidized bed reactor operation, the catalyst may be a particle and the particle shape may be spherical. The spherical catalyst could be prepared by any method known to those skilled in the art. Preferably, the spherical catalyst may be prepared via spray drying of zeolite containing sols of appropriate concentration and composition. The zeolite containing sol may optionally contain binder. The spherical catalyst particle may have a predominant particle size or diameter that makes it suitable for a particular reactor type, such as a fluidized bed reactor. The spherical particle diameter of the catalyst is preferably selected to be in the range of 20-500 microns. More preferably, the spherical catalyst may have a particle diameter in the range of 50-200 microns.

[0031] According to an implementation of the disclosed subject matter, the methane-containing gas stream conversion and corresponding benzene yield per pass are higher than the conversion and yield obtained with the same aromatization catalyst and under the same methane-containing gas aromatization conditions, but in the absence of a hydrogen acceptor in the reaction zone of the aromatization reactor. The hydrogen acceptor used in this reaction can be any metal-containing alloy or a compound that has the ability, when subjected to aromatization operating conditions, to selectively accept or react with hydrogen to form a sufficiently strong hydrogen-acceptor bond. The hydrogen acceptor preferably reversibly binds the hydrogen in such a way that during operation in the aromatization reactor the hydrogen is strongly bound to the acceptor under the methane-containing gas stream aromatization conditions. In addition, the hydrogen acceptor is preferably able to release the hydrogen when transported to the regeneration section where it is subjected to a different set of (regeneration) conditions that favor release of the previously bound hydrogen and regeneration of the hydrogen acceptor. The hydrogen

acceptor could be a particle(s) in the form of cylindrical pellets, rings, spheres, a monolithic structure, a porous net-shaped structure, and the like.

[0032] Suitable hydrogen acceptors metals include: Ti, Zr, V, Nb, Hf, Mg, La, Th, Sc as well as other transition metals, elements or compounds or mixtures thereof. The

hydrogen acceptor may comprise metals that exhibit magnetic properties, such as for example Fe, Co or Ni or various ferro-, para- or dimagnetic alloys of these metals. One or more hydrogen acceptors that exhibit appropriate particle sizes and mass for fluidized bed aromatization operation may be used in the reaction zone to achieve the desired degree of hydrogen separation and removal.

[0033] According to an implementation of the disclosed subject matter, the hydrogen acceptor includes a palladium barrier layer surrounding at least a portion of the outer surface of the hydrogen acceptor. In an embodiment, the palladium barrier layer may surround the entire outer surface of the hydrogen acceptor. For example, the outer surface of the hydrogen acceptor may be fully covered by a continuous palladium barrier layer.

The palladium barrier layer may have a thickness of ≤ 1000 nm, ≤ 100 nanometer, and $\leq$ than 10 nanometer. Figure 3 shows an example of a cross section of a palladium-coated hydrogen acceptor particle 300. As shown, a hydrogen acceptor particle 310 may include a palladium barrier layer 320 surrounding the outer surface of the hydrogen acceptor 310.

[0034] The palladium barrier layer is effective in avoiding reactions of the metal of the hydrogen acceptor with hydrocarbons during the aromatization reaction or other, non-hydrocarbon species present in the methane containing gas stream as well as with gases present during the regeneration of the hydrogen acceptor (e.g., nitrogen, steam, oxygen, etc.). For example, the palladium barrier layer is effective in avoiding reactions between the hydrogen acceptor and non-hydrogen species. In particular, the palladium barrier layer is only hydrogen permeable thereby allowing only hydrogen to pass through the palladium layer, either inwards or outwards through the palladium barrier layer and thereby avoids contact of the hydrogen acceptor metal(s) with non-hydrogen species. Non-hydrogen species are species that may potentially react with the hydrogen acceptor and include oxygen containing species, nitrogen, hydrocarbons, but excluding noble gases.

[0035] The mixing of both types of particles, i.e., catalyst particles and hydrogen acceptor particles, provides for the quick removal of the produced hydrogen from the reaction zone and for shifting the aromatization reaction equilibrium toward greater methane-containing gas conversion and benzene yields per pass. This mixing of both types

of particles can be achieved in a variety of aromatization reactor configurations.

According to an embodiment of the disclosed subject matter, the aromatization reactor may be any type of reactor such as a fluidized bed reactor, a fixed bed reactor, a moving bed reactor, and the like. Based on the type of reactor utilized, the size, shape, and

5 arrangement of the hydrogen acceptor and/or catalyst may be selected to maximize the efficiency of the aromatization reaction and process conditions. For example, in an aromatization reactor that is a fluidized bed reactor, the hydrogen acceptor may be a particle having a particle size in the range of 2-100 microns, 10-90 microns, 20-80 microns, and 40-60 microns. As another example, in an aromatization reactor that is a
10 fixed bed reactor, the hydrogen acceptor may be a particle having a particle size in the range of greater than about 100 microns to 100 mm, 200 micron to 50 mm, 500 micron to 10 mm, and 800 micron to 3 mm. Yet another advantage of the presently disclosed subject matter is that the shapes, sizes and mass of both the hydrogen acceptor and the aromatization catalyst may be designed and selected in such a way so that can be co-
15 fluidized in the aromatization reactor to form a fluidized bed, if desired. Also, the disclosed subject matter provides for two or more different hydrogen acceptors (e.g., different by chemical formula and/or physical properties) to be simultaneously used with the aromatization catalyst in the aromatization reactor to achieve the desired degree of hydrogen separation from the aromatization reaction zone.

20 **[0036]** According to an implementation of the disclosed subject matter, a single composite particle may include the aromatization catalyst and the hydrogen acceptor. Fig. 4 shows an example of a single composite particle which may combine the aromatization catalyst and the hydrogen acceptor. In particular, Fig. 4 shows a cross section of a single particle combining the aromatization catalyst with the hydrogen acceptor and the layer of
25 palladium surrounding the hydrogen acceptor. As shown in Fig. 4, a single composite particle 400 may include a hydrogen acceptor 410. A palladium barrier layer 420 may surround the hydrogen acceptor 410. Further, aromatization catalyst particles 430 may be fixed and/or deposited on the palladium barrier layer 420. For example, the catalyst particle might be spray-dried onto the hydrogen acceptor. As another example, the catalyst
30 particles may be dispersed in a fluid, mixed with the hydrogen acceptor particles, and then the fluid can be vaporized. In an embodiment, a single composite particle including the aromatization catalyst and hydrogen acceptor may be implemented in a fixed-bed type of aromatization reactor.

[0037] An implementation of the disclosed subject matter provides for a hydrogen acceptor that is a porous net-shaped structure through which the methane-containing gas stream and aromatization catalyst may flow in the reaction zone. This type of reactor has been referred to by those skilled in the art as a gas-flowing solids-fixed bed reactor (GFSFBR). An example of this implementation is shown in Fig. 5. As shown, a hydrogen acceptor 510 may be a porous net-shaped structure. The hydrogen acceptor 510 may be surrounded by a palladium barrier layer 520. In particular, the hydrogen acceptor 510 may be surrounded by the palladium barrier layer 520, and combined, may be a porous net-shaped structure that is an open, porous structure (e.g., such as a wire structure or a monolith). Accordingly, because the hydrogen acceptor 510 and surrounding palladium barrier layer 520 form a porous net-shaped structure, the methane-containing gas stream (not shown) and aromatization catalyst 530 may move and flow through the net-shaped structure that may be fixed and/or disposed in an aromatization reactor. In a similar implementation (although not shown in a Figure), the aromatization catalyst may be a porous net-shaped structure through which the methane-containing gas stream and hydrogen acceptor may flow in the reaction zone. For example, the aromatization catalyst may be a porous net-shaped structure that is an open, porous structure (e.g., such as a wire structure or a monolith). In this case, the methane-containing gas stream and palladium-coated hydrogen acceptor particles (e.g., see the hydrogen acceptor particle shown in Fig. 3) may move and flow through the aromatization catalyst having a net-shaped structure that may be fixed and/or disposed in an aromatization reactor.

[0038] According to an implementation of the disclosed subject matter, when the aromatization reactor is a fixed bed reactor, the fixed bed reactor may be operated in a swing mode. As an example, the process for converting a methane-containing gas stream to aromatics (e.g., conversion of methane to benzene, or "M2B") may take place in a conventional fixed bed reactor that may be filled with catalyst and hydrogen acceptor particles (e.g., see Fig. 2). For example, both catalyst and hydrogen acceptor particles may occupy 30% of the aromatization reactor volume and the remaining 40% being void space (this does not include the volume of a cooling/heating system). In general, the M2B process converts methane to benzene and hydrogen, and the hydrogen acceptor particles may absorb and subsequently store hydrogen as a hydride, e.g., in the case of a zirconium hydrogen acceptor, the hydrogen may be stored in the zirconium hydrogen acceptor particle as zirconium hydride.

[0039] In the example above, the space velocity of methane used may be 1000 NI/(liter catalyst * hour) (i.e., ratio of the gas volume flow, in normal liters per hour, and the catalyst volume). As an example, with a conversion of 100%, the following results may be achieved: STY(Benzene) = 580 grams / (liter catalyst * h); and STY(Hydrogen) = 135
5 grams / (liter catalyst * h). STY is the space time yield; the mass of product per unit time and per unit catalyst volume. In the example, the storage capacity of ZrH₂ equals 120g H₂/liter of ZrH₂. According to this example, the M2B reaction may run for slightly less than 1 hour (e.g., 0.89 hours or 53 minutes) before the hydrogen acceptor particle (which were initially empty) may be fully loaded. In general, fully loaded means all of the
10 hydrogen acceptor has been converted to a metal-hydride (e.g., Zr has been converted to ZrH₂). In practice, however, full conversion may not be achieved.

[0040] After 1 hour of operation the hydrogen acceptor particle may be fully loaded, e.g., a zirconium hydrogen acceptor particle may have absorbed the produced hydrogen by forming ZrH₂. At this point, the flow of methane to the reactor may be stopped and
15 methane containing feed stream is changed to a sweep gas stream. The sweep gas stream is a non-hydrocarbon gas stream fed to the reactor to remove hydrogen, e.g., the hydrogen being released by the dehydrogenation of the hydrogen acceptor via the reaction of ZrH₂ to Zr and gaseous H₂, from the reactor. Next, energy has to be supplied to the reactor to desorb the hydrogen from ZrH₂. The regeneration energy is about 85 kJ/gram of H₂, which
20 corresponds to about 10 MJ/liter catalyst as defined above. This energy may be supplied by an exothermal reaction like a partial oxidation of the hydrogen to be released from the hydrogen acceptor via reaction with oxygen present in the sweep gas. A regeneration time of approximately 1 hour may be selected. It may be beneficial to regenerate the hydrogen acceptor particle at a temperature close to the M2B reaction temperature (in this example
25 700°C). The hydrogen partial pressure generated by releasing the hydrogen from the hydrogen acceptor may be around 0.3 bar and a suitable sweep gas may be employed. In general, higher temperatures yield higher hydrogen pressures. Next, the M2B process may be started again by switching the composition of the gas feed to the aromatization reactor from the sweep gas to the methane containing feed stream and continuing the reaction.

[0041] In general, the M2B process is a self-limiting process. The M2B reaction in
30 combination with storage of hydrogen as a hydride, such as ZrH₂, is an exothermic process and therefore does not require heating. In case the aromatization reactor temperature rises due to the heat released, the reaction automatically stops. This is due to the fact that the

hydrogen acceptor, e.g., zirconium, may no longer absorb hydrogen in case the equilibrium pressure at a given temperature is above the hydrogen pressure generated by the M2B reaction. As a consequence, the overall reaction switches to the conventional strongly endothermic M2B reaction and the reactor cools. For the case described above, the temperature may not rise above 850°C.

[0042] Another important advantage of the process of this invention is that it provides for the aromatization catalyst and the hydrogen acceptor to be withdrawn from the reaction zone of the aromatization reactor and regenerated. According to an implementation, the process may further provide for continuously regenerating the catalyst to remove coke formed during the reaction and continuously regenerating the hydrogen acceptor by releasing the hydrogen under regeneration conditions. In an implementation, the catalyst and hydrogen acceptor may be regenerated in a single regeneration vessel. In another implementation, the catalyst and hydrogen acceptor may be regenerated in separate vessels. As an example, the aromatization catalyst and hydrogen acceptor may be regenerated in separate vessel or vessels according to one of the schemes illustrated in Figures 6 and 7 and then continuously returned back to the aromatization reactor for continuous aromatics and hydrogen production. The hydrogen acceptor and catalyst regeneration could be accomplished either simultaneously or stepwise in the same vessel as illustrated in Figure 6 or separately in separate vessels as illustrated in Figure 7. This later operation scheme provides for maximum flexibility to accomplish the hydrogen release or regeneration of the acceptor and catalyst under different and suitable for the purpose set of operating conditions. The regeneration of catalyst and hydrogen acceptor could be accomplished in fixed, moving or fluidized bed reactor vessels schematically shown in Figures 6 and 7.

[0043] In Figure 6, regenerator vessel 600 is used to regenerate the catalyst and regenerate the hydrogen acceptor. The catalyst and hydrogen acceptor are introduced via inlet 602 and are then removed via outlet 604. Hydrogen removed from the hydrogen acceptor and gases produced by catalyst regeneration are removed from the regenerator via one or more outlets (not shown). As an example, the aromatization conditions may comprise a first pressure and the regeneration conditions may comprise a second pressure, and the first pressure may be different from the second pressure, i.e., the pressure used under aromatization conditions may be different from the pressure used under regeneration conditions. For example, the first pressure (i.e., aromatization condition pressure) may be higher than the second pressure (i.e., regeneration condition pressure). According to an

embodiment, the first pressure (i.e., aromatization condition pressure) may be about 20 barg and the second pressure (i.e., regeneration condition pressure) may be about 3 barg, and of course another pressure may be selected for each of the aromatization conditions and regeneration conditions. Similarly, the aromatization conditions may include a first temperature and the regeneration conditions may include a second temperature, and the first temperature may be different from the second temperature, i.e., the temperature used under aromatization conditions may be different from the temperature used under regeneration conditions. For example, the first temperature (i.e., aromatization condition temperature) may be lower than the second temperature (i.e., regeneration condition temperature). According to an embodiment, the first temperature (i.e., aromatization condition temperature) may be about 700°C and the second temperature (i.e., regeneration condition temperature) may be about 800°C, and of course another temperature may be selected for each of the aromatization conditions and regeneration conditions. In an embodiment, an isobaric and/or isothermal aromatization-regeneration may be performed by simply changing the feed gas composition from a methane-containing gas stream to a non-hydrocarbon containing gas stream, such as nitrogen. According to an implementation, a change to the pressure and/or temperature between the aromatization conditions and regeneration conditions may allow for regeneration of both the aromatization catalyst and hydrogen acceptor, in the same vessel, or in different vessels.

20 **[0044]** According to an implementation, the aromatization catalyst and hydrogen acceptor may each be regenerated under different regeneration conditions, as shown for example in Figure 7. In Figure 7, regenerator system 700 comprises a separation step 702 to separate the catalyst from the hydrogen acceptor that is fed from the reactor via line 704. The catalyst is fed to catalyst regeneration vessel 706, and the hydrogen acceptor is fed to hydrogen acceptor regeneration vessel 708. The catalyst and hydrogen acceptor are then mixed back together in mixing step 710 and then fed back to the reactor via line 712.

25 **[0045]** In the case of separate regeneration (e.g., see Figure 3), the hydrogen acceptor particles could be separated from the catalyst on the basis of (but not limited to) differences in mass, particle size, density or on the basis of difference in magnetic properties between the acceptor and the catalyst particles. In the latter case, the hydrogen acceptor according to an implementation could be selected from the group of materials exhibiting ferro-, para- or diamagnetic properties and comprising Fe, Co or Ni.

30

[0046] It is well known that, the methane-containing gas aromatization catalysts form coke during the reaction. Accumulation of coke on the surface of the catalyst gradually covers the active aromatization sites of the catalyst resulting in gradual reduction of its activity. Therefore, the coked catalyst has to be removed at certain carefully chosen frequencies from the reaction zone of the aromatization reactor and regenerated in one of the regeneration vessels depicted in Figures 6 and 7. The regeneration of the catalyst can be carried out by any method known to those skilled in the art. For example, two possible regeneration methods are hot hydrogen stripping and oxidative burning at temperatures sufficient to remove the coke from the surface of the catalyst. If hot hydrogen stripping is used to regenerate the catalyst, then at least a portion of the hydrogen used for the catalyst regeneration may come from the hydrogen released from the hydrogen acceptor. Additionally, fresh hydrogen may be fed to the catalyst regeneration vessel as needed to properly supplement the hydrogen released from the hydrogen acceptor and to complete the catalyst regeneration. If the regeneration is carried out in the same vessel (e.g., see Figure 6), then the hydrogen removed from the hydrogen acceptor in-situ could at least partially hydrogen strip and regenerate the catalyst. If the regeneration is carried out in different vessels (e.g., see Figure 7) the operating conditions of each vessel could be selected and maintained to favor the regeneration of the catalyst or the hydrogen acceptor. Hydrogen removed from the hydrogen acceptor could then again be used to at least partially hydrogen strip and regenerate the catalyst.

[0047] Yet another important advantage of the process of the disclosed subject matter over the prior art is that it provides for the release of the hydrogen that is bound to the hydrogen acceptor when the saturated acceptor is subjected to a specific set of conditions in the regeneration vessel(s). Furthermore, the released hydrogen could be utilized to regenerate the catalyst or subjected to any other suitable chemical use or monetized to improve the overall aromatization process economics.

[0048] Another important advantage of the disclosed subject matter is that it allows for different regeneration conditions to be used in the different regeneration vessel or vessels to optimize and minimize the regeneration time required for the catalyst and hydrogen acceptor and to improve performance in the aromatization reaction.

[0049] The aforementioned advantages of the process of the disclosed subject matter provide for an efficient removal of hydrogen from the reaction zone of methane-containing gas aromatization reactor operating in fluidized bed mode and for shifting the reaction

equilibrium towards higher methane-containing gas stream conversion and benzene yields per pass. Therefore, the disclosed subject matter has the potential to allow for the commercialization of an economically attractive direct, non-oxidative methane-containing gas stream aromatization process.

CLAIMS

1. A process for the aromatization of a methane-containing gas stream comprising:
contacting the methane-containing gas stream in a reaction zone of an
aromatization reactor comprising an aromatization catalyst and a hydrogen acceptor under
5 methane-containing gas aromatization conditions to produce reaction products comprising
aromatics and gaseous hydrogen, wherein at least a portion of the gaseous hydrogen
produced is bound by the hydrogen acceptor in the reaction zone and removed from the
reaction products and the reaction zone, and
wherein the hydrogen acceptor comprises a palladium barrier layer surrounding at
10 least a portion of the outer surface of the hydrogen acceptor.
2. The process of claim 1, wherein the methane-containing gas stream conversion and
corresponding benzene yield per pass are higher than the conversion and yield obtained
with the same aromatization catalyst and under the same methane-containing gas
aromatization conditions, but in the absence of a hydrogen acceptor in the reaction zone of
15 the aromatization reactor.
3. The process of claim 1, wherein the methane-containing gas stream comprises at
least 60 % vol. methane.
4. The process of claim 1, wherein the aromatization catalyst comprises a zeolite
selected from the group consisting of ZSM-5, ZSM-22, ZSM-8, ZSM-11, ZSM-12 or
20 ZSM-35.
5. The process of claim 1, wherein the aromatization catalyst comprises a metal
selected from the group consisting of vanadium, chromium, manganese, zinc, iron, cobalt,
nickel, copper, gallium, germanium, niobium, molybdenum, ruthenium, rhodium, silver,
tantalum, tungsten, rhenium, platinum and lead and mixtures thereof.
- 25 6. The process of claim 1, wherein the hydrogen acceptor comprises a metal or metals
that are capable of selectively binding hydrogen under the methane-containing gas
aromatization conditions in the reaction zone.
7. The process of claim 1, wherein the hydrogen acceptor comprises a metal selected
from the group consisting of Ti, Zr, V, Nb, Hf, Mg, La, Th, Sc and other transition metals
30 and compounds or mixtures thereof.
8. The process of claim 1, wherein the palladium barrier layer is effective in avoiding
reactions between the hydrogen acceptor and non-hydrogen species.
9. The process of claim 1, wherein the aromatization reactor is a fluidized bed reactor.

10. The process of claim 9, wherein the hydrogen acceptor is a particle having a particle size in the range of 2-100 microns.
11. The process of claim 1, wherein the aromatization reactor is a fixed bed reactor.
12. The process of claim 11, wherein the hydrogen acceptor is a particle having a particle size in the range of greater than about 100 microns and less than about 100 mm.
13. The process of claim 11, wherein the fixed bed reactor is operated in a swing mode.
14. The process of claim 1, wherein the hydrogen acceptor is a porous net-shaped structure through which the methane-containing gas stream and aromatization catalyst may flow in the reaction zone.
15. The process of claim 1, wherein the aromatization catalyst is a porous net-shaped structure through which the methane-containing gas stream and hydrogen acceptor may flow in the reaction zone.
16. The process of claim 1, wherein the palladium barrier layer has a thickness of $\leq$ 1000 nm.
17. The process of claim 1, wherein a single composite particle comprises the aromatization catalyst and the hydrogen acceptor.
18. The process of claim 1, further comprising continuously regenerating the catalyst to remove coke formed during the reaction and continuously regenerating the hydrogen acceptor by releasing the hydrogen under regeneration conditions.
19. The process of claim 18, wherein the catalyst and hydrogen acceptor are regenerated in a single regeneration vessel.
20. The process of claim 18, wherein the catalyst and hydrogen acceptor are regenerated in separate vessels.

Figure 1

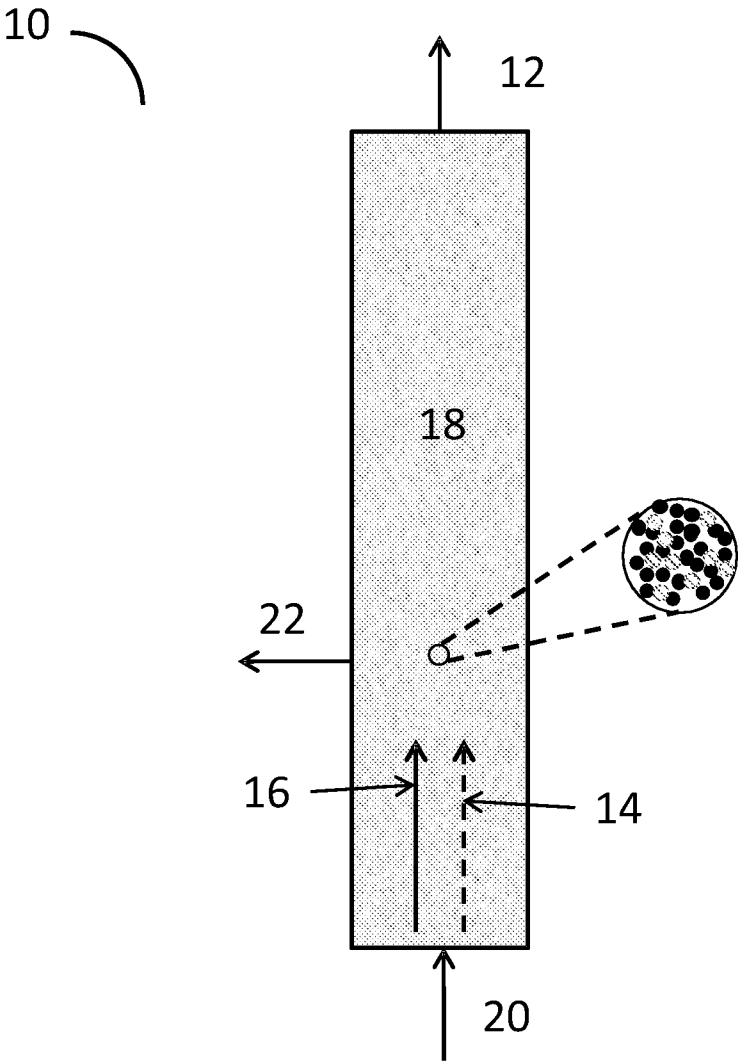
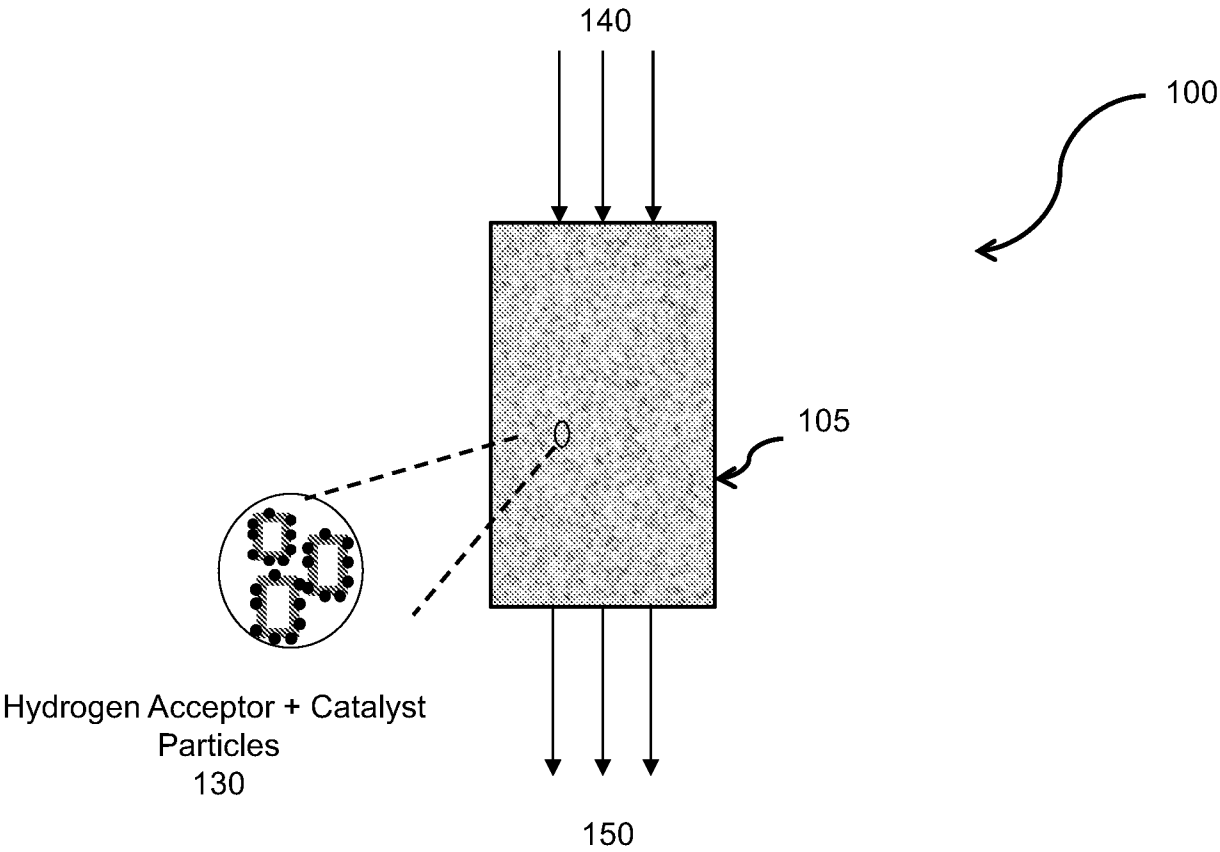


Figure 2



3/7

Figure 3

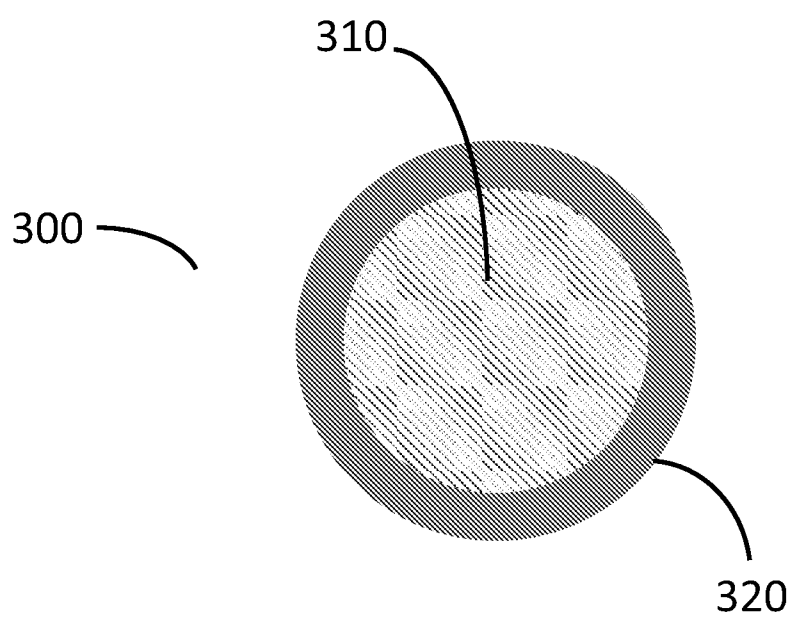


Figure 4

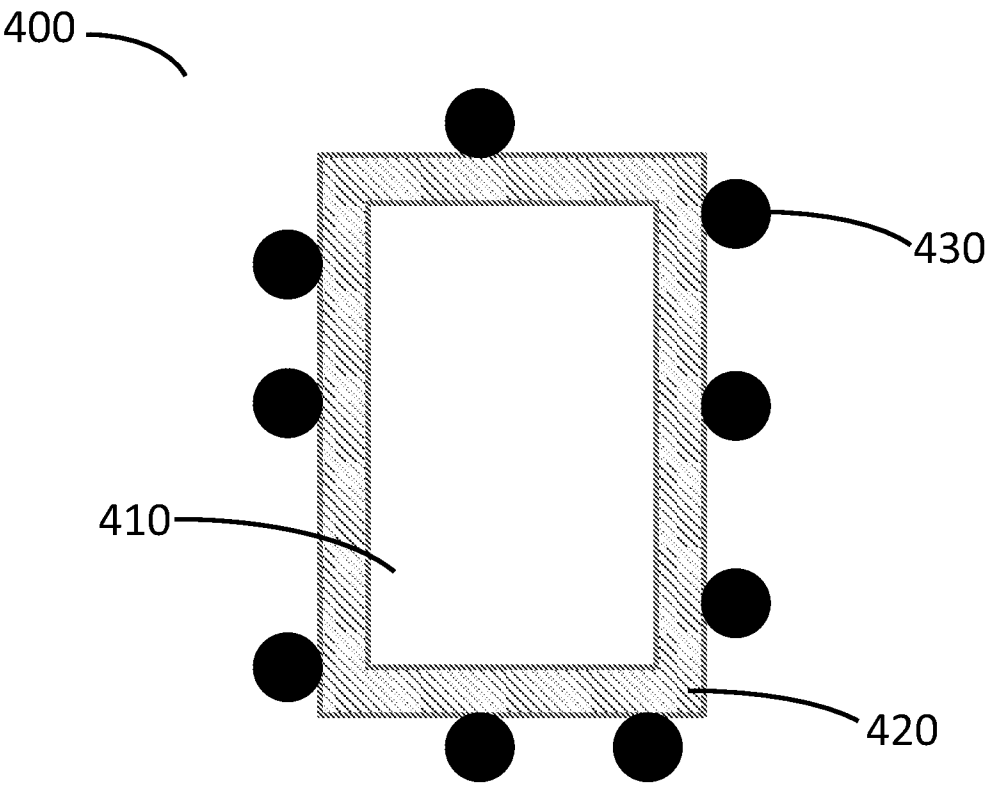


Figure 5

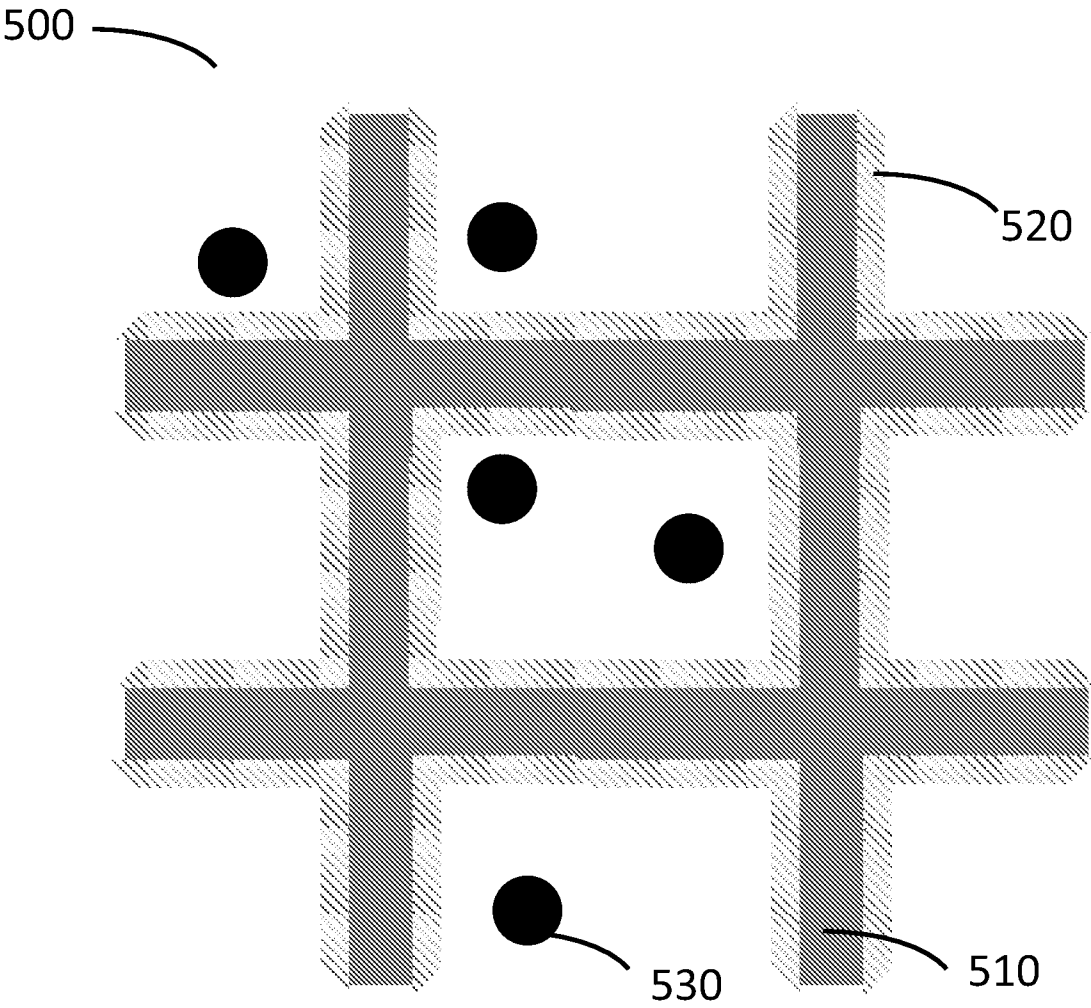


Figure 6

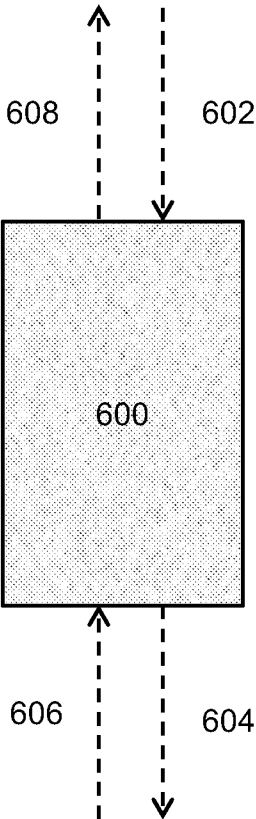
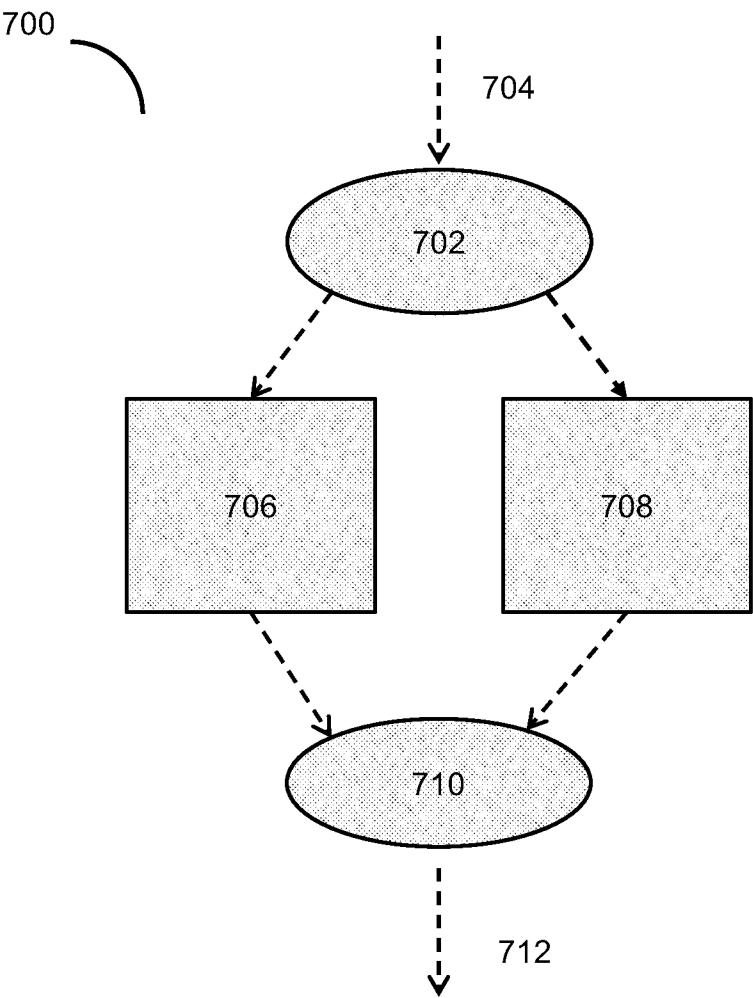


Figure 7



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US16/35968

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01D 53/04; C01B 3/38 (2016.01)

CPC - B01D 53/04, C01B 3/38, 3/40

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8): B01D 53/04, 53/047, 53/12; B01J 8/02, 8/08, 8/24, 21/20, 23/44; C01B 3/38; C07C 2/84 (2016.01)

CPC: B01D 53/04, 53/047, 53/12; B01J 8/02, 8/08, 8/24, 21/20, 23/44; C01B 3/38, 3/40; C07C 2/84

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

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

Patseer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, INPADOC Data); EBSCO; Wiley Interscience; Google Scholar/Patent; methane, natural gas, hydrocarbon, reactor, reformer, fluidized or fixed bed, catalyst, zeolite, ZSM, sieve, palladium, pd, coat, barrier, layer, hydrogen acceptor, remove, absorb, dehydrogenation, aromatic, benzene, toluene, xylene

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2015/0099914 A1 (SHELL OIL COMPANY) 09 April 2015; figures 2-3; paragraphs [0009], [0012]-[0014], [0017], [0019], [0021]-[0023]; claims 5-9, 11	1-20
Y	(PRASAD, P et al.) Novel Circulating Fluidized-Bed Membrane Reformer for the Efficient Production of Ultraclean Fuels from Hydrocarbons. Industrial & Engineering Chemistry Research. 2002. vol. 41; page 6519, column 2, Hydrogen Permselective Membranes; page 6520, column 1, Hydrogen Permselective Membranes	1-15, 17-20
Y	US 4,496,373 A (BEHR, F et al.) 29 January 1985; abstract; column 2, lines 36-42	1, 16
Y	AU 2011/290935 B2 (BASF SE) 23 February 2012; abstract; page 9, lines 31-32	10
Y	WO 2015/052297 A1 (PROTIA AS) 16 April 2015; page 1, lines 4-10; page 19, lines 15-23; page 20, lines 17-23; page 21, lines 1-5; page 22, lines 1-4; page 25, lines 1-2	11-14, 17
A	US 2012/0028794 A1 (LAM, KT et al.) 02 February 2012; entire document	1-20
A	US 2010/0205863 A1 (BIOLLAZ, S et al.) 19 August 2010; entire document	1-20
A	US 2007/0172419 A1 (PENG, XD et al.) 26 July 2007; entire document	1-20
A	US 4,929,792 A (DESSAU, RM) 29 May 1990; entire document	1-20

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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"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

31 July 2016 (31.07.2016)

Date of mailing of the international search report

09 SEP 2016

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Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
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Shane Thomas

PCT Helpdesk: 571-272-4300
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