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

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
27 February 2014 (27.02.2014)

WIPO | PCT

(10) **International Publication Number**
WO 2014/031315 A1

(51) **International Patent Classification**:
C10G 9/00 (2006.01) ***C07C 7/12*** (2006.01)
C07C 11/24 (2006.01) ***B01J 19/10*** (2006.01)
C07C 2/76 (2006.01)

(21) **International Application Number**:
PCT/US2013/053541

(22) **International Filing Date**:
5 August 2013 (05.08.2013)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
61/691,322 21 August 2012 (21.08.2012) US
13/950,475 25 July 2013 (25.07.2013) US

(71) **Applicant**: **UOP LLC** [US/US]; 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US).

(72) **Inventors**: **RENDE, Dean E.**; UOP LLC, 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US). **GORAWARA, Jayant K.**; UOP LLC, 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US). **COUGHLIN, Peter K.**; UOP LLC, 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (US).

(74) **Agent**: **GOLDBERG, Mark**; UOP LLC, 25 East Algonquin Road, P. O. Box 5017, Des Plaines, Illinois 60017-5017 (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, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, 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, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(54) **Title**: HYDRIDE REMOVAL AND METHANE CONVERSION PROCESS USING A SUPERSONIC FLOW REACTOR

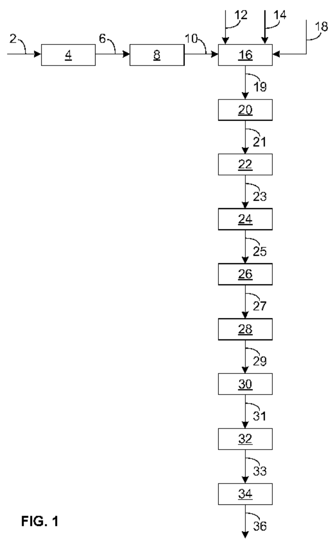


FIG. 1

(57) **Abstract**: Methods and systems are provided for converting methane in a feed stream to acetylene. The method includes removing at least a portion of hydrides of arsenic, phosphorus, antimony, silicon, and boron from a hydrocarbon stream. The hydrocarbon stream is introduced into a supersonic reactor and pyrolyzed to convert at least a portion of the methane to acetylene. The reactor effluent stream may be treated to convert acetylene to another hydrocarbon process. The method according to certain aspects includes controlling the level of hydrides of arsenic, phosphorus, antimony, silicon, and boron in the hydrocarbon stream.

WO 2014/031315 A1

HYDRIDE REMOVAL AND METHANE CONVERSION PROCESS USING A SUPERSONIC FLOW REACTOR

PRIORITY CLAIM OF EARLIER NATIONAL APPLICATIONS

[0001] This application claims priority to U.S. Application No. 61/691,322 filed August 21, 2012 and U.S. Application No. 13/950,475 filed July 25, 2013.

BACKGROUND OF THE INVENTION

[0002] A process is disclosed for removing contaminants from a process stream and converting methane in the process stream to acetylene using a supersonic flow reactor. More particularly, a process is provided for removal of trace contaminants including hydrides of arsenic, phosphorus, antimony, silicon, and boron from the process stream. This process can be used in conjunction with other contaminant removal processes including mercury removal, oxygenate removal including water and CO_2 removal, and removal of sulfur containing compounds containing these impurities from the process stream.

[0003] Light olefin materials, including ethylene and propylene, represent a large portion of the worldwide demand in the petrochemical industry. Light olefins are used in the production of numerous chemical products via polymerization, oligomerization, alkylation and other well-known chemical reactions. Producing large quantities of light olefin material in an economical manner, therefore, is a focus in the petrochemical industry. These light olefins are essential building blocks for the modern petrochemical and chemical industries. The main source for these materials in present day refining is the steam cracking of petroleum feeds.

[0004] The cracking of hydrocarbons brought about by heating a feedstock material in a furnace has long been used to produce useful products, including for example, olefin products. For example, ethylene, which is among the more important products in the chemical industry, can be produced by the pyrolysis of feedstocks ranging from light paraffins, such as ethane and propane, to heavier fractions such as naphtha. Typically, the lighter feedstocks produce higher ethylene yields (50-55% for ethane compared to 25-30% for naphtha); however, the cost of the feedstock is more likely to determine which is used. Historically, naphtha cracking has provided the largest source of ethylene, followed by ethane and propane pyrolysis, cracking, or dehydrogenation. Due to the large demand for ethylene and other light olefinic materials, however, the cost of these traditional feeds has steadily increased.

[0005] Energy consumption is another cost factor impacting the pyrolytic production of chemical products from various feedstocks. Over the past several decades, there have been significant improvements in the efficiency of the pyrolysis process that have reduced the costs of production. In a typical or conventional pyrolysis plant, a feedstock passes through a plurality of heat exchanger tubes where it is heated externally to a pyrolysis temperature by the combustion products of fuel oil or natural gas and air. One of the more important steps taken to minimize production costs has been the reduction of the residence time for a feedstock in the heat exchanger tubes of a pyrolysis furnace. Reduction of the residence time increases the yield of the desired product while reducing the production of heavier by-products that tend to foul the pyrolysis tube walls. However, there is little room left to improve the residence times or overall energy consumption in traditional pyrolysis processes.

[0006] More recent attempts to decrease light olefin production costs include utilizing alternative processes and/or feed streams. In one approach, hydrocarbon oxygenates and more specifically methanol or dimethylether (DME) are used as an alternative feedstock for producing light olefin products. Oxygenates can be produced from available materials such as coal, natural gas, recycled plastics, various carbon waste streams from industry and various products and by-products from the agricultural industry. Making methanol and other oxygenates from these types of raw materials is well established and typically includes one or more generally known processes such as the manufacture of synthesis gas using a nickel or cobalt catalyst in a steam reforming step followed by a methanol synthesis step at relatively high pressure using a copper-based catalyst.

[0007] Once the oxygenates are formed, the process includes catalytically converting the oxygenates, such as methanol, into the desired light olefin products in an oxygenate to olefin (OTO) process. Techniques for converting oxygenates, such as methanol to light olefins (MTO), are described in US 4,387,263, which discloses a process that utilizes a catalytic conversion zone containing a zeolitic type catalyst. US 4,587,373 discloses using a zeolitic catalyst like ZSM-5 for purposes of making light olefins. US 5,095,163; US 5,126,308 and US 5,191,141 on the other hand, disclose an MTO conversion technology utilizing a non-zeolitic molecular sieve catalytic material, such as a metal aluminophosphate (ELAPO) molecular sieve. OTO and MTO processes, while useful, utilize an indirect process for forming a desired hydrocarbon product by first converting a feed to an oxygenate and subsequently converting the oxygenate to the hydrocarbon product. This indirect route of production is often associated with energy and cost penalties, often reducing the advantage gained by using a less expensive feed material.

[0008] Recently, attempts have been made to use pyrolysis to convert natural gas to ethylene. US 7,183,451 discloses heating natural gas to a temperature at which a fraction is converted to hydrogen and a hydrocarbon product such as acetylene or ethylene. The product stream is then quenched to stop further reaction and subsequently reacted in the presence of a catalyst to form liquids to be transported. The liquids ultimately produced include naphtha, gasoline, or diesel. While this method may be effective for converting a portion of natural gas to acetylene or ethylene, it is estimated that this approach will provide only a 40% yield of acetylene from a methane feed stream. While it has been identified that higher temperatures in conjunction with short residence times can increase the yield, technical limitations prevent further improvement to this process in this regard.

[0009] While the foregoing traditional pyrolysis systems provide solutions for converting ethane and propane into other useful hydrocarbon products, they have proven either ineffective or uneconomical for converting methane into these other products, such as, for example ethylene. While MTO technology is promising, these processes can be expensive due to the indirect approach of forming the desired product. Due to continued increases in the price of feeds for traditional processes, such as ethane and naphtha, and the abundant supply and corresponding low cost of natural gas and other methane sources available, for example the more recent accessibility of shale gas, it is desirable to provide commercially feasible and cost effective ways to use methane as a feed for producing ethylene and other useful hydrocarbons.

[0010] In the process of the present invention, it has been found important to minimize the concentration of water as well as carbon monoxide and carbon dioxide to avoid the occurrence of a water shift reaction which may result in undesired products being produced as well as reduce the quantity of the desired acetylene. Other contaminants should be removed for environmental, production or other reasons including the repeatability of the process. Since variations in the hydrocarbon stream being processed in accordance with this invention may result in product variations, it is highly desired to have consistency in the hydrocarbon stream even when it is provided from different sources. Natural gas wells from different regions will produce natural gas of differing compositions with anywhere from a few percent carbon dioxide up to a majority of the volume being carbon dioxide and the contaminant removal system will need to be designed to deal with such different compositions.

[0011] In addition to well-known contaminants such as hydrogen sulfide, carbonyl sulfide and mercaptans, hydrocarbon feedstocks often contain a small quantity of arsine. Usually arsine is present to the extent of only several hundred parts per billion (ppb) by weight. However, even this small amount is normally beyond the allowable limits of an acceptable product (typically less than 20 ppb). The presence of arsine, even at very low concentrations, reduces the polymer yield of olefin catalysts significantly. For example as disclosed in US 4,861,939, at 20°C., 15 bar, WHSV of 6 kg/kg-hr, Ziegler-type catalyst when 305 ppb ArH_3 is present, the yield was 10,000 kg polypropylene per kilogram of catalyst, while when there was less than 3 ppb of ArH_3, the yield was 32,000 kg polypropylene per kilogram of catalyst. Arsine is a powerful reducing agent, which appears able to reduce a olefin polymerization catalysts and cause their deactivation. As a result, there has been a real need for removing arsine from hydrocarbons, especially those used for polymer production.

[0012] The purification of propylene and other olefin feed streams is particularly complicated by the small difference between the boiling points of propylene and arsine which hampers arsine removal by fractionation. Consequently, the levels of arsine impurity in propylene stocks are often intolerably high.

[0013] The hydrides of boron, silicon, arsenic, phosphorus and antimony are known to be severe catalyst poisons in a variety of processes, including the manufacture of polypropylene and polyethylene. There are other hydrides, including metal hydrides and organometallic hydrides that also act as catalyst poisons. The polymerization reactions to make polypropylene and polyethylene occur over high activity Ziegler-Natta type catalysts or the newly developed metallocene single site catalysts. In order to provide the best catalytic activity of these catalysts, the feed olefin and any other hydrocarbon streams, such as comonomer streams, must be free of contaminants that can bond to the transitional metal groups on the catalyst, thus deactivating the catalyst. The metallocenes are extremely sensitive to arsine and phosphine with sensitivity to levels in the parts per billion (ppb) level range. Most polypropylene manufacturers specify extremely low levels of arsine and phosphine contamination in their propylene supplies with specifications set anywhere from 5 to 50 ppb of either of these impurities. Even the traditional Ziegler-type catalysts, which are less sensitive to these impurities, will produce greatly increased yields upon the removal of the impurities from the propylene. The same issues are present in the manufacture of various other polymers, including polyethylene, polystyrene and various elastomers.

[0014] In addition to removal of arsine and phosphines, it is important to remove sulfur compounds. There have been extensive previous efforts to develop adsorbents for the purification of propylene and other hydrocarbons.

[0015] US 3,782,076 discloses a process for reducing the arsenic content, believed to be present as arsine, from gaseous hydrocarbon streams by contacting said streams with supported lead oxide. However, the presence of sulfur compounds is said to interfere with the removal of arsine, and furthermore the supported lead oxide may not be regenerated when sulfur compounds are present in the feed.

[0016] US 3,833,498 discloses a process for reducing the arsenic content, believed to be present as ***arsine,*** from gaseous hydrocarbon streams by contacting said streams with activated carbon derived from a bituminous coal and containing cobalt, nickel, molybdenum and vanadium. However, the feed should be substantially dry and free of sulfur compounds.

[0017] US 5,330,560 discloses a process for recovery of arsenic from a gas, such as natural gas, using an inert solid support coated with phosphoric acid and a metal halide, such as ferric chloride or cupric chloride.

[0018] US 5,302,771 describes the use of a modified alumina to remove impurities from liquid hydrocarbon streams, such as propylene. The alumina is impregnated with a metal selected from lithium, potassium, calcium, magnesium, barium and sodium.

[0019] US 5,990,372 discloses an adsorbent for removal of trace amounts of sulfur, mercury, arsenic, metal hydrides and mixtures thereof, where the adsorbent is a combination of iron oxide, manganese oxide and a support material.

[0020] US 6,033,556 discloses the use of a capture mass comprising an alumina support with a metal oxide or sulfide. Metals used included copper, molybdenum, tungsten, iron, nickel and cobalt. The capture masses were used to trap heavy metals, including arsenic, mercury and lead.

[0021] US 4,744,221 discloses a method of storing and delivering arsine by contacting a zeolite having a pore size between 5 to 15 angstroms with arsine, at a temperature between -30°C and 30°C and then heating the arsine-adsorbed zeolite to a temperature not greater than 175°C to release a portion of the arsine.

[0022] US 5,704,965 discloses a fluid storage and delivery system using a carbon sorbent material that has an affinity for a variety of fluid reagents, including arsine and phosphine.

[0023] There is a need for materials to remove the arsine and phosphine from hydrocarbon streams as well as the sulfur impurities and oxygenates, especially in light of the intolerance of the polymerization catalysts for these impurities. In particular, there remains a need to overcome the difficulty caused by sulfur compounds being adsorbed and limiting the capacity for the adsorbents to remove arsine and phosphines which, while present in much smaller concentrations than the sulfur compounds, must still be removed from the hydrocarbon stream used in a process for making chemicals from methane containing hydrocarbon streams.

SUMMARY OF THE INVENTION

[0024] According to one aspect of the invention is provided a method for producing acetylene. The method generally includes introducing a feed stream portion of a hydrocarbon stream including methane into a supersonic reactor. The method also includes pyrolyzing the methane in the supersonic reactor to form a reactor effluent stream portion of the hydrocarbon stream including acetylene. The method further includes treating at least a portion of the hydrocarbon stream in a contaminant removal zone to remove contaminants comprising hydrides of arsenic, phosphorus, antimony, silicon, and boron containing these impurities from the process stream.

[0025] According to another aspect of the invention a method for controlling contaminant levels in a hydrocarbon stream in the production of acetylene from a methane feed stream is provided. The method includes introducing a feed stream portion of a hydrocarbon stream including methane into a supersonic reactor. The method also includes pyrolyzing the methane in the supersonic reactor to form a reactor effluent stream portion of the hydrocarbon stream including acetylene. The method further includes maintaining the concentration level of hydrides of arsenic, phosphorus, antimony, silicon, and boron from the process stream in at least a portion of the process stream to below specified levels.

[0026] According to yet another aspect of the invention is provided a system for producing acetylene from a methane feed stream. The system includes a supersonic reactor for receiving a methane feed stream and configured to convert at least a portion of methane in the methane feed stream to acetylene through pyrolysis and to emit an effluent stream including the acetylene. The system also includes a hydrocarbon conversion zone in communication with the supersonic reactor and configured to receive the effluent stream and convert at least a portion of the acetylene therein to another hydrocarbon compound in a product stream. The system includes a hydrocarbon stream line for transporting the methane feed stream, the reactor effluent stream, and the product stream. The system further includes a contaminant removal zone in communication with the hydrocarbon stream line for removing hydrides of arsenic, phosphorus, antimony, silicon, and boron from the process stream from one or more of the methane feed stream, the effluent stream, and the product stream.

[0027] A single layer to specifically remove the hydrides listed as contaminants here may be used. It is also contemplated that the invention would include the use of multi-layer adsorbent beds to remove other contaminants. In accordance with one embodiment of the invention is also provided a multi-layer adsorbent bed for purification of hydrocarbons, comprising a guard layer of sulfur and/or sulfur containing compounds removal adsorbent, and at least one layer of adsorbent to remove hydrides including boron, silicon, arsenic, phosphorus, antimony and other hydrides. The arsenic hydrides are normally present in the highest concentrations. Oxygenates, including water, methanol and carbon dioxide as well as organic oxygen containing compounds such as alcohols, ethers, esters, ketones, aldehydes are also removed within the multi-layer adsorbent bed. The oxygenates and sulfur containing compounds removal layer may be zeolite 13X or 5A or other appropriate adsorbent, and the arsine/phosphine and other hydrides removal layer may be a transition metal oxide on a support, such as alumina, clay or other inert solid. In one embodiment of the invention, the arsine/phosphine removal layer comprises a metal oxide such as CuO. In another embodiment, the arsine/phosphine removal layer comprises a highly dispersed CuO on alumina such that an X-ray of the CuO on alumina does show a considerably reduced CuO diffraction pattern compared to a typical CuO diffraction pattern. Water is a byproduct of the hydride removal and is also a contaminant that needs to be removed from the hydrocarbon stream. The water removal layer can be a variety of adsorbents, such as zeolite 3A

[0028] In another embodiment of the invention, the arsine/phosphine removal layer and the oxygenate removal layer are combined, either by an admixture of the two adsorbents or by use of a hybrid adsorbent. However, the sulfur removal layer preferably remains separate from the arsine/phosphine removal layer due to the tendency for the adsorption of the sulfur to block adsorption of arsine and phosphine and other hydrides. It is also contemplated within the scope of the present invention, that more than one adsorbent layer may be employed to remove hydrides.

[0029] In yet another embodiment of the invention, the sulfur removal layer and the oxygenate and water removal layer can be thermally regenerated, while the arsine/phosphine removal layer, although non-regenerable, is subject to the regeneration conditions at which the other layers are regenerated. This regeneration can be completed by continued passage of a heated gas through these layers after removal of the water, other oxygenates, and sulfur compounds has been essentially completed.

BRIEF DESCRIPTION OF THE DRAWING

[0030] The FIGURE shows the flow scheme for a process of producing a hydrocarbon product by use of a supersonic reactor with one or more contaminant removal zones employed in the process.

DETAILED DESCRIPTION

[0031] One proposed alternative to the previous methods of producing olefins that has not gained much commercial traction includes passing a hydrocarbon feedstock into a supersonic reactor and accelerating it to supersonic speed to provide kinetic energy that can be transformed into heat to enable an endothermic pyrolysis reaction to occur. Variations of this process are set out in US 4,136,015 and US 4,724,272, and SU 392723A. These processes include combusting a feedstock or carrier fluid in an oxygen-rich environment to increase the temperature of the feed and accelerate the feed to supersonic speeds. A shock wave is created within the reactor to initiate pyrolysis or cracking of the feed.

[0032] More recently, US 5,219,530 and US 5,300,216 have suggested a similar process that utilizes a shock wave reactor to provide kinetic energy for initiating pyrolysis of natural gas to produce acetylene. More particularly, this process includes passing steam through a heater section to become superheated and accelerated to a nearly supersonic speed. The heated fluid is conveyed to a nozzle which acts to expand the carrier fluid to a supersonic speed and lower temperature. An ethane feedstock is passed through a compressor and heater and injected by nozzles to mix with the supersonic carrier fluid to turbulently mix together at a Mach 2.8 speed and a temperature of 427°C. The temperature in the mixing section remains low enough to restrict premature pyrolysis. The shockwave reactor includes a pyrolysis section with a gradually increasing cross-sectional area where a standing shock wave is formed by back pressure in the reactor due to flow restriction at the outlet. The shock wave rapidly decreases the speed of the fluid, correspondingly rapidly increasing the temperature of the mixture by converting the kinetic energy into heat. This immediately initiates pyrolysis of the ethane feedstock to convert it to other products. A quench heat exchanger then receives the pyrolized mixture to quench the pyrolysis reaction.

[0033] Methods and systems for converting hydrocarbon components in methane feed streams using a supersonic reactor are generally disclosed. As used herein, the term "methane feed stream" includes any feed stream comprising methane. The methane feed streams provided for processing in the supersonic reactor generally include methane and form at least a portion of a process stream that includes at least one contaminant. The methods and systems presented herein remove or convert the contaminant in the process stream and convert at least a portion of the methane to a desired product hydrocarbon compound to produce a product stream having a reduced contaminant level and a higher concentration of the product hydrocarbon compound relative to the feed stream. By one approach, a hydrocarbon stream portion of the process stream includes the contaminant and methods and systems presented herein remove or convert the contaminant in the hydrocarbon stream.

[0034] The term "hydrocarbon stream" as used herein refers to one or more streams that provide at least a portion of the methane feed stream entering the supersonic reactor as described herein or are produced from the supersonic reactor from the methane feed stream, regardless of whether further treatment or processing is conducted on such hydrocarbon stream. The "hydrocarbon stream" may include the methane feed stream, a supersonic reactor effluent stream, a desired product stream exiting a downstream hydrocarbon conversion process or any intermediate or by-product streams formed during the processes described herein. The hydrocarbon stream may be carried via a process stream. The term "process stream" as used herein includes the "hydrocarbon stream" as described above, as well as it may include a carrier fluid stream, a fuel stream, an oxygen source stream, or any streams used in the systems and the processes described herein.

[0035] Prior attempts to convert light paraffin or alkane feed streams, including ethane and propane feed streams, to other hydrocarbons using supersonic flow reactors have shown promise in providing higher yields of desired products from a particular feed stream than other more traditional pyrolysis systems. Specifically, the ability of these types of processes to provide very high reaction temperatures with very short associated residence times offers significant improvement over traditional pyrolysis processes. It has more recently been realized that these processes may also be able to convert methane to acetylene and other useful hydrocarbons, whereas more traditional pyrolysis processes were incapable or inefficient for such conversions.

[0036] The majority of previous work with supersonic reactor systems, however, has been theoretical or research based, and thus has not addressed problems associated with practicing the process on a commercial scale. In addition, many of these prior disclosures do not contemplate using supersonic reactors to effectuate pyrolysis of a methane feed stream, and tend to focus primarily on the pyrolysis of ethane and propane. One problem that has recently been identified with adopting the use of a supersonic flow reactor for light alkane pyrolysis, and more specifically the pyrolysis of methane feeds to form acetylene and other useful products therefrom, includes negative effects that particular contaminants in commercial feed streams can create on these processes and/or the products produced therefrom. Previous work has not considered contaminants and the need to control or remove specific contaminants, especially in light of potential downstream processing of the reactor effluent stream.

[0037] The term “adsorption” as used herein encompasses the use of a solid support to remove atoms, ions or molecules from a gas or liquid. The adsorption may be by “physisorption” in which the adsorption involves surface attractions or “chemisorptions” where there are actual chemical changes in the contaminant that is being removed. Depending upon the particular adsorbent, contaminant and stream being purified, the adsorption process may be regenerative or nonregenerative. Either pressure swing adsorption, temperature swing adsorption or displacement processes may be employed in regenerative processes. A combination of these processes may also be used. The adsorbents may be any porous material known to have application as an adsorbent including carbon materials such as activated carbon clays, molecular sieves including zeolites and metal organic frameworks (MOFs), metal oxides including silica gel and aluminas that are promoted or activated, , as well as other porous materials that can be used to remove or separate contaminants.

[0038] “Pressure swing adsorption (PSA)” refers to a process where a contaminant is adsorbed from a gas when the process is under a relatively higher pressure and then the contaminant is removed or desorbed thus regenerating the adsorbent at a lower pressure.

[0039] “Temperature swing adsorption (TSA)” refers to a process where regeneration of the adsorbent is achieved by an increase in temperature such as by sending a heated gas through the adsorbent bed to remove or desorb the contaminant. Then the adsorbent bed is often cooled before resumption of the adsorption of the contaminant.

[0040] “Displacement” refers to a process where the regeneration of the adsorbent is achieved by desorbing the contaminant with another liquid that takes its place on the adsorbent. Such as process is shown in US 8,211,312 in which a feed and a desorbent are applied at different locations along an adsorbent bed along with withdrawals of an extract and a raffinate. The adsorbent bed functions as a simulated moving bed. A circulating adsorbent chamber fluid can simulate a moving bed by changing the composition of the liquid surrounding the adsorbent. Changing the liquid can cause different chemical species to be adsorbed on, and desorbed from, the adsorbent. As an example, initially applying the feed to the adsorbent can result in the desired compound or extract to be adsorbed on the adsorbent, and subsequently applying the desorbent can result in the extract being desorbed and the desorbent being adsorbed. In such a manner, various materials may be extracted from a feed. In some embodiments of the present invention, a displacement process may be employed.

[0041] In accordance with various embodiments disclosed herein, therefore, processes and systems for removing or converting contaminants in methane feed streams are presented. The removal of particular contaminants and/or the conversion of contaminants into less deleterious compounds has been identified to improve the overall process for the pyrolysis of light alkane feeds, including methane feeds, to acetylene and other useful products. In some instances, removing these compounds from the hydrocarbon or process stream has been identified to improve the performance and functioning of the supersonic flow reactor and other equipment and processes within the system. Removing these contaminants from hydrocarbon or process streams has also been found to reduce poisoning of downstream catalysts and adsorbents used in the process to convert acetylene produced by the supersonic reactor into other useful hydrocarbons, for example hydrogenation catalysts that may be used to convert acetylene into ethylene. Still further, removing certain contaminants from a hydrocarbon or process stream as set forth herein may facilitate meeting product specifications.

[0042] In accordance with one approach, the processes and systems disclosed herein are used to treat a hydrocarbon process stream, to remove one or more contaminants therefrom and convert at least a portion of methane to acetylene. The hydrocarbon process stream described herein includes the methane feed stream provided to the system, which includes methane and may also include ethane or propane. The methane feed stream may also include combinations of methane, ethane, and propane at various concentrations and may also include other hydrocarbon compounds. In one approach, the hydrocarbon feed stream includes natural gas. The natural gas may be provided from a variety of sources including, but not limited to, gas fields, oil fields, coal fields, fracking of shale fields, biomass, and landfill gas. In another approach, the methane feed stream can include a stream from another portion of a refinery or processing plant. For example, light alkanes, including methane, are often separated during processing of crude oil into various products and a methane feed stream may be provided from one of these sources. These streams may be provided from the same refinery or different refinery or from a refinery off gas. The methane feed stream may include a stream from combinations of different sources as well.

[0043] In accordance with the processes and systems described herein, a methane feed stream may be provided from a remote location or at the location or locations of the systems and methods described herein. For example, while the methane feed stream source may be located at the same refinery or processing plant where the processes and systems are carried out, such as from production from another on-site hydrocarbon conversion process or a local natural gas field, the methane feed stream may be provided from a remote source via pipelines or other transportation methods. For example a feed stream may be provided from a remote hydrocarbon processing plant or refinery or a remote natural gas field, and provided as a feed to the systems and processes described herein. Initial processing of a methane stream may occur at the remote source to remove certain contaminants from the methane feed stream. Where such initial processing occurs, it may be considered part of the systems and processes described herein, or it may occur upstream of the systems and processes described herein. Thus, the methane feed stream provided for the systems and processes described herein may have varying levels of contaminants depending on whether initial processing occurs upstream thereof.

[0044] In one example, the methane feed stream has a methane content ranging from 50 to 100 mol%. In another example, the concentration of methane in the hydrocarbon feed ranges from 70 to 100 mol% of the hydrocarbon feed. In yet another example, the concentration of methane ranges from 90 to 100 mol% of the hydrocarbon feed.

[0045] In one example, the concentration of ethane in the methane feed ranges from 0 to 30 mol% and in another example from 0 to 10 mol%. In one example, the concentration of propane in the methane feed ranges from 0 to 10 mol% and in another example from 0 to 2 mol%.

[0046] The methane feed stream may also include heavy hydrocarbons, such as aromatics, paraffinic, olefinic, and naphthenic hydrocarbons. These heavy hydrocarbons if present will likely be present at concentrations of between 0 mol% and 100 mol%. In another example, they may be present at concentrations of between 0 mol% and 10 mol% and may be present at between 0 mol% and 2 mol%.

[0047] The present invention relates to the removal of arsenic hydride, often referred to as arsine in its most frequently occurring form, from light olefin-containing hydrocarbon streams. It further relates to the removal of other hydrides, including phosphorus hydrides, antimony hydrides, silicon hydrides and boron hydrides. The hydride removal process of the present invention reduces the arsine concentration in the treated hydrocarbon feedstock to 20 parts per billion by weight (ppb) and preferably 5-10 ppb or lower with similar reduction in the concentration of other hydrides that may be present in a hydrocarbon stream. The original arsine concentration in the feedstock may be as high as 1000 parts per million by weight (ppm) or higher depending on the process of manufacture, as well as depending upon the origin of the hydrocarbon feedstock. Similar reductions in the concentration of other hydrides is achieved by this invention. In most cases the source of hydrides including arsenic hydrides will be from the hydrocarbon feed and removal should be done upstream of the supersonic reactor.

[0048] In one embodiment of the invention, the copper oxide was well dispersed on an alumina support. At the highly dispersed levels of copper oxide employed herein, X-ray comparison of test samples did show a reduced intensity of the x-ray peaks for CuO while standard prior art compositions did show more intense doublet X-ray peaks at 35.5 and 38.8 angle 2 theta. It was found that better copper dispersion leads to better utilization of the copper with more arsine adsorbed per unit weight adsorbent than would otherwise be found. Smaller adsorber vessels may then be used with lower costs for capital outlays.

[0049] Oxygenates, including water, methanol and carbon dioxide also need to be removed. Water is produced as a byproduct to the removal of the arsine and other hydrides and needs to be removed from the hydrocarbon feedstock as well. While feedstock oxygenate removal can be accomplished in the same portion of the bed as sulfur containing compound removal, a bed of a water removing material may also be provided at the effluent end of the arsine adsorbent, preferably a 3A type bed.

[0050] In one embodiment, the hydrocarbon feedstock is purified by passage through a multi-layer bed. There are a minimum of two beds, with one bed for the removal of sulfur and or sulfur compounds and at least a second bed for the removal of hydrides as well as water. In the preferred embodiment of the invention the hydrocarbon will first pass through a layer for oxygenate and sulfur containing compound removal, comprising a layer of zeolites including various ion exchange forms, including transition metals, preferably zinc. The zeolites that can be used include faujasites (13X, CaX, NaY, CaY, ZnX), chabazites, clinoptilolites and LTA (4A, 5A) zeolites.

[0051] Another type of layer for oxygenate and sulfur containing compound removal that is effective in the practice of the present invention is a promoted alumina. The promoter is selected from one or more alkali metals or alkaline earth metals. The preferred alkali metals include sodium and potassium and the preferred alkaline earth metals include magnesium and calcium. The next layer is an adsorbent for arsine, phosphine, antimony hydride and other hydrides, also operating as a guard bed. The preferred materials for this hydride guard bed are active metal oxides which are broadly defined as including transition metal oxides, such as copper oxides and manganese oxide and other transition metal oxides as well as zinc oxide and lead oxide. Particularly favorable results were found with copper oxide.

[0052] In another embodiment of the present invention, the function of the arsine/phosphine removal layer and the water removal layer may be combined into a single layer. This would be done either by using a mixture of the arsine/phosphine removal material and the water removal material or by use of a hybrid or composite type material. It would be a simpler operation with only two adsorbents required. A high surface area support for the arsine adsorbent may be used for the purpose of water removal. The arsine/phosphine removal layer then functions also as a water removal layer. Once water is produced by the hydride reaction with the metal component, the water is immediately scavenged by the support.

[0053] By one aspect, the hydrocarbon stream includes one or more contaminants including hydrides of arsenic, phosphorus, antimony, silicon, and boron and sulfur and oxygenates and compounds containing these impurities. While the systems and processes are described generally herein with regard to removing these contaminants from a hydrocarbon stream, it should be understood that these contaminants may also be removed from other portions of the process stream. The hydrocarbon stream contaminant according to one aspect includes one or more contaminants selected from hydrides of arsenic, phosphorus, antimony, silicon, and boron and sulfur and oxygenates and compounds containing these impurities

[0054] According to one aspect, the contaminants in the hydrocarbon stream may be naturally occurring in the feed stream, such as, for example, present in a natural gas source. According to another aspect, the contaminants may be added to the hydrocarbon stream during a particular process step. In accordance with another aspect, the contaminant may be formed as a result of a specific step in the process, such as a product or by-product of a particular reaction, such as oxygen or carbon dioxide reacting with a hydrocarbon to form an oxygenate.

[0055] The process for forming acetylene from the methane feed stream described herein utilizes a supersonic flow reactor for pyrolyzing methane in the feed stream to form acetylene. The supersonic flow reactor may include one or more reactors capable of creating a supersonic flow of a carrier fluid and the methane feed stream and expanding the carrier fluid to initiate the pyrolysis reaction. In one approach, the process may include a supersonic reactor as generally described in US 4,724,272, which is incorporated herein by reference, in their entirety. In another approach, the process and system may include a supersonic reactor such as described as a "shock wave" reactor in US 5,219,530 and US 5,300,216, which are incorporated herein by reference, in their entirety. In yet another approach, the supersonic reactor described as a "shock wave" reactor may include a reactor such as described in "Supersonic Injection and Mixing in the Shock Wave Reactor" Robert G. Cerff, University of Washington Graduate School, 2010.

[0056] While a variety of supersonic reactors may be used in the present process, an exemplary reactor will have a supersonic reactor that includes a reactor vessel generally defining a reactor chamber. While the reactor will often be found as a single reactor, it should be understood that it may be formed modularly or as separate vessels. A combustion zone or chamber is provided for combusting a fuel to produce a carrier fluid with the desired temperature and flowrate. The reactor may optionally include a carrier fluid inlet for introducing a supplemental carrier fluid into the reactor. One or more fuel injectors are provided for injecting a combustible fuel, for example hydrogen, into the combustion chamber. The same or other injectors may be provided for injecting an oxygen source into the combustion chamber to facilitate combustion of the fuel. The fuel and oxygen are combusted to produce a hot carrier fluid stream typically having a temperature of from 1200° to 3500°C in one example, between 2000° and 3500°C in another example, and between 2500° and 3200°C in yet another example. According to one example the carrier fluid stream has a pressure of 1 atm or higher, greater than 2 atm in another example, and greater than 4 atm in another example.

[0057] The hot carrier fluid stream from the combustion zone is passed through a converging-diverging nozzle to accelerate the flowrate of the carrier fluid to above Mach 1.0 in one example, between Mach 1.0 and Mach 4.0 in another example, and between Mach 1.5 and Mach 3.5 in another example. In this regard, the residence time of the fluid in the reactor portion of the supersonic flow reactor is between 0.5 and 100 ms in one example, 1.0 and 50 ms in another example, and 1.5 and 20 ms in another example.

[0058] A feedstock inlet is provided for injecting the methane feed stream into the reactor to mix with the carrier fluid. The feedstock inlet may include one or more injectors for injecting the feedstock into the nozzle, a mixing zone, an expansion zone, or a reaction zone or a chamber. The injector may include a manifold, including for example a plurality of injection ports.

[0059] In one approach, the reactor may include a mixing zone for mixing of the carrier fluid and the feed stream. In another approach, no mixing zone is provided, and mixing may occur in the nozzle, expansion zone, or reaction zone of the reactor. An expansion zone includes a diverging wall to produce a rapid reduction in the velocity of the gases flowing therethrough, to convert the kinetic energy of the flowing fluid to thermal energy to further heat the stream to cause pyrolysis of the methane in the feed, which may occur in the expansion section and/or a downstream reaction section of the reactor. The fluid is quickly quenched in a quench zone to stop the pyrolysis reaction from further conversion of the desired acetylene product to other compounds. Spray bars may be used to introduce a quenching fluid, for example water or steam into the quench zone.

[0060] The reactor effluent exits the reactor via the outlet and as mentioned above forms a portion of the hydrocarbon stream. The effluent will include a larger concentration of acetylene than the feed stream and a reduced concentration of methane relative to the feed stream. The reactor effluent stream may also be referred to herein as an acetylene stream as it includes an increased concentration of acetylene. The acetylene may be an intermediate stream in a process to form another hydrocarbon product or it may be further processed and captured as an acetylene product stream. In one example, the reactor effluent stream has an acetylene concentration prior to the addition of quenching fluid ranging from 4 to 60 mol%. In another example, the concentration of acetylene ranges from 10 to 50 mol% and from 15 to 47 mol% in another example.

[0061] In one example, the reactor effluent stream has a reduced methane content relative to the methane feed stream ranging from 10 to 90 mol%. In another example, the concentration of methane ranges from 30 to 85 mol% and from 40 to 80 mol% in another example.

[0062] In one example the yield of acetylene produced from methane in the feed in the supersonic reactor is between 40 and 95 mol%. In another example, the yield of acetylene produced from methane in the feed stream is between 50 and 90 mol%. Advantageously, this provides a better yield than the estimated 40% yield achieved from previous, more traditional, pyrolysis approaches.

[0063] By one approach, the reactor effluent stream is reacted to form another hydrocarbon compound. In this regard, the reactor effluent portion of the hydrocarbon stream may be passed from the reactor outlet to a downstream hydrocarbon conversion process for further processing of the stream. While it should be understood that the reactor effluent stream may undergo several intermediate process steps, such as, for example, water removal, adsorption, and/or absorption to provide a concentrated acetylene stream, these intermediate steps will not be described in detail herein except where particularly relevant to the present invention.

[0064] The reactor effluent stream having a higher concentration of acetylene may be passed to a downstream hydrocarbon conversion zone where the acetylene may be converted to form another hydrocarbon product. The hydrocarbon conversion zone may include a hydrocarbon conversion reactor for converting the acetylene to another hydrocarbon product. While in one embodiment the invention involves a process for converting at least a portion of the acetylene in the effluent stream to ethylene through hydrogenation in a hydrogenation reactor, it should be understood that the hydrocarbon conversion zone may include a variety of other hydrocarbon conversion processes instead of or in addition to a hydrogenation reactor, or a combination of hydrocarbon conversion processes. Similarly the process and equipment as discussed herein may be modified or removed and not intended to be limiting of the processes and systems described herein. Specifically, it has been identified that several other hydrocarbon conversion processes, other than those disclosed in previous approaches, may be positioned downstream of the supersonic reactor, including processes to convert the acetylene into other hydrocarbons, including, but not limited to: alkenes, alkanes, methane, acrolein, acrylic acid, acrylates, acrylamide, aldehydes, polyacetylides, benzene, toluene, styrene, aniline, cyclohexanone, caprolactam, propylene, butadiene, butyne diol, butandiol,

C_2-C_4 hydrocarbon compounds, ethylene glycol, diesel fuel, diacids, diols, pyrrolidines, and pyrrolidones.

[0065] A contaminant removal zone for removing one or more contaminants from the hydrocarbon or process stream may be located at various positions along the hydrocarbon or process stream depending on the impact of the particular contaminant on the product or process and the reason for the contaminants removal, as described further below. For example, particular contaminants have been identified to interfere with the operation of the supersonic flow reactor and/or to foul components in the supersonic flow reactor. Thus, according to one approach, a contaminant removal zone is positioned upstream of the supersonic flow reactor in order to remove these contaminants from the methane feed stream prior to introducing the stream into the supersonic reactor. Other contaminants have been identified to interfere with a downstream processing step or hydrocarbon conversion process, in which case the contaminant removal zone may be positioned upstream of the supersonic reactor or between the supersonic reactor and the particular downstream processing step at issue. Still other contaminants have been identified that should be removed to meet particular product specifications. Where it is desired to remove multiple contaminants from the hydrocarbon or process stream, various contaminant removal zones may be positioned at different locations along the hydrocarbon or process stream. In still other approaches, a contaminant removal zone may overlap or be integrated with another process within the system, in which case the contaminant may be removed during another portion of the process, including, but not limited to the supersonic reactor or the downstream hydrocarbon conversion zone. This may be accomplished with or without modification to these particular zones, reactors or processes. While the contaminant removal zone is often positioned downstream of the hydrocarbon conversion reactor, it should be understood that the contaminant removal zone in accordance herewith may be positioned upstream of the supersonic flow reactor, between the supersonic flow reactor and the hydrocarbon conversion zone, or downstream of the hydrocarbon conversion zone or along other streams within the process stream, such as, for example, a carrier fluid stream, a fuel stream, an oxygen source stream, or any streams used in the systems and the processes described herein.

[0066] In one approach, a method includes removing a portion of contaminants from the hydrocarbon stream. In this regard, the hydrocarbon stream may be passed to the contaminant removal zone. In one approach, the method includes controlling the contaminant concentration in the hydrocarbon stream. The contaminant concentration may be controlled by maintaining the concentration of contaminant in the hydrocarbon stream to below a level that is tolerable to the supersonic reactor or a downstream hydrocarbon conversion process. In one approach, the contaminant concentration is controlled by removing at least a portion of the contaminant from the hydrocarbon stream. As used herein, the term removing may refer to actual removal, for example by adsorption, absorption, or membrane separation, or it may refer to conversion of the contaminant to a more tolerable compound, or both. In one example, the contaminant concentration is controlled to maintain the level of contaminant in the hydrocarbon stream to below a harmful level. In another example, the contaminant concentration is controlled to maintain the level of contaminant in the hydrocarbon stream to below a lower level. In yet another example, the contaminant concentration is controlled to maintain the level of contaminant in the hydrocarbon stream to below an even lower level.

[0067] The FIGURE provides a flow scheme for an embodiment of the invention. In the FIGURE, a hydrocarbon feed 2, such as methane, is shown entering a first contaminant removal zone 4, then passing through line 6 to one or more heaters 8. A heated hydrocarbon feed 10 then enters a supersonic reactor 16 together with fuel 12, oxidizer 14 and optional steam 18. In the supersonic reactor, a product stream containing acetylene is produced. The product stream 19 from supersonic reactor 16 may then go to a second contaminant removal zone 20, through line 21 to a compression and adsorption/separation zone 22. If further purification is necessary, the stream passes through line 23 into a third contaminant removal zone 24. A purified acetylene stream 25 is sent to hydrocarbon conversion zone 26 to be converted into one or more hydrocarbon products which contain one or more impurities. These one or more hydrocarbon products 27 are shown being sent to a separation zone 28, then through line 29 to fourth contaminant removal zone 30, then through line 31 to a polishing reactor 32 to convert unreacted acetylene to the one or more hydrocarbon products. The now purified product stream 33 is sent to a product separation zone 34 and the primary product stream 36 is shown exiting at the bottom. Secondary products may also be produced. While there is a single contaminant removal zone shown in four locations in the FIGURE, each single contaminant removal zone may comprise one or more separate beds or other contaminant removal apparatus. In some embodiments of the invention, there may be fewer contaminant removal zones depending upon the quality of the hydrocarbon feed 2, product stream 19 and primary product stream 36.

[0068] While there have been illustrated and described particular embodiments and aspects, it will be appreciated that numerous changes and modifications will occur to those skilled in the art, and it is intended in the appended claims to cover all those changes and modifications which fall within the true spirit and scope of the present disclosure and appended claims.

CLAIMS:

1. A method for producing acetylene comprising:

introducing a feed stream portion of a hydrocarbon stream comprising methane into a supersonic reactor;

pyrolyzing the methane in the supersonic reactor to form a reactor effluent stream portion of the hydrocarbon stream comprising acetylene; and

treating at least a portion of the hydrocarbon stream in a contaminant removal zone to remove hydrides of arsenic, phosphorus, antimony, silicon, and boron from the hydrocarbon stream is contacted with an adsorbent material comprising one or more active metal oxides to remove said hydrides of arsenic, phosphorus, antimony, silicon, and boron.

2. The method of claim 1 further comprising treating said at least a portion of the hydrocarbon stream to remove other contaminants.

3. The method of claim 1 wherein said zeolite is selected from the group consisting of faujasites (13X, CaX, NaY, CaY, and ZnX), chabazites, clinoptilolites and LTA (3A, 4A, 5A) zeolites.

4. The method of claim 1 wherein said active metal oxide is selected from the group consisting of copper oxide, manganese oxide, lead oxide and zinc oxide.

5. The method of claim 1 wherein the contaminant comprises a compound selected from the group consisting of arsines and phosphines.

6. The method of claim 1 wherein the contaminant removal zone is positioned upstream of the supersonic reactor to remove the portion of the hydrides of arsenic, phosphorus, antimony, silicon, and boron and sulfur and oxygenates from the hydrocarbon stream prior to introducing the process stream into the supersonic reactor.

7. The method of claim 1 further comprising passing the reactor effluent stream to a downstream hydrocarbon conversion zone and converting at least a portion of the acetylene in the reactor effluent stream to another hydrocarbon in the hydrocarbon conversion zone.

8. The method of claim 7 wherein the contaminant removal zone is positioned downstream of the supersonic reactor and upstream of the hydrocarbon conversion zone to remove the at least portion of the hydrides of arsenic, phosphorus, antimony, silicon, and boron from the hydrocarbon stream prior to introducing the effluent stream portion thereof into hydrocarbon conversion zone.

9. The method of claim 3 wherein the zeolite is Zn-X, said transition metal oxide adsorbent is copper oxide and said layer to adsorb water is a 3A type zeolite.

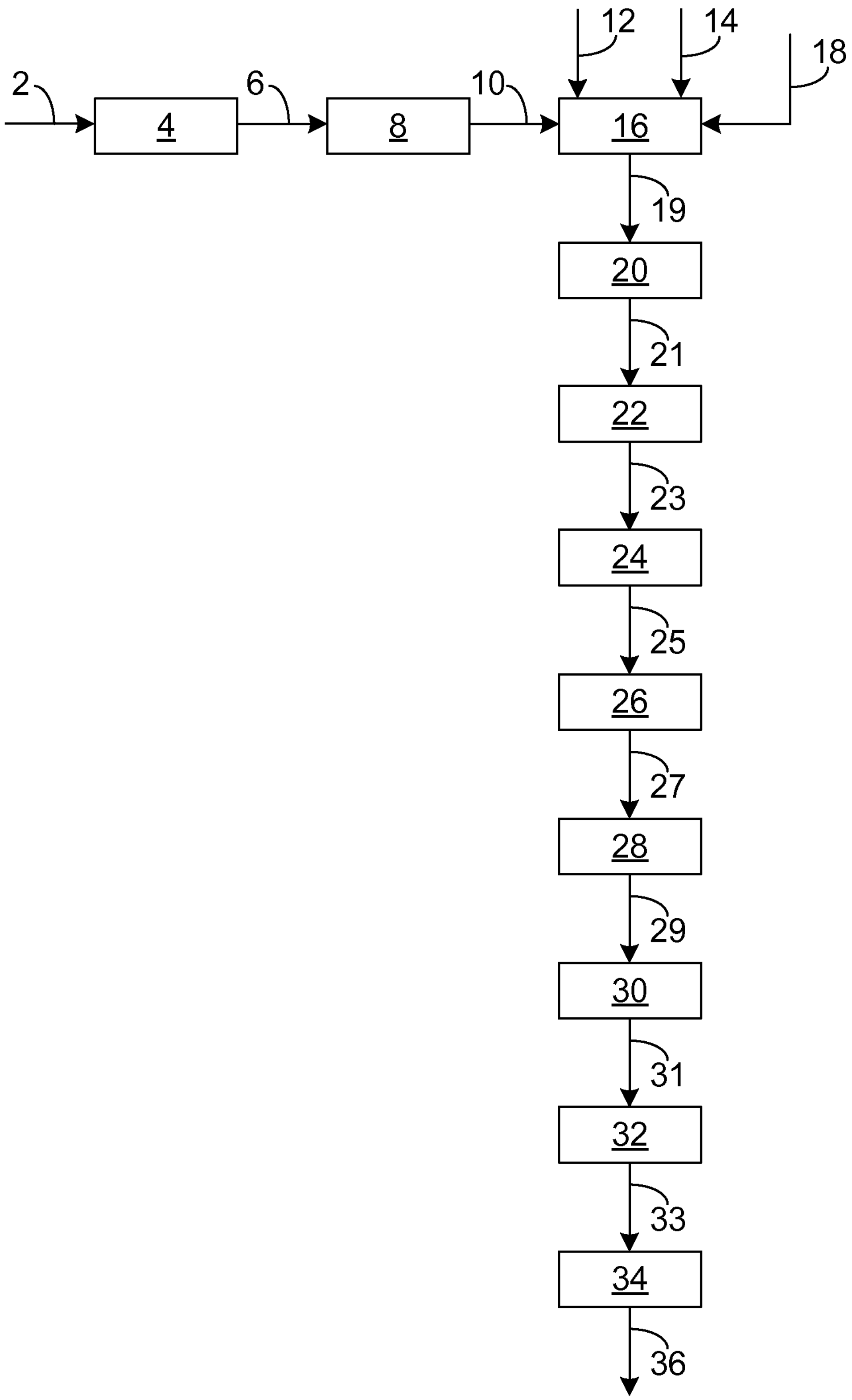
10. A system for producing acetylene from a methane feed stream comprising:

a supersonic reactor for receiving a methane feed stream and configured to convert at least a portion of methane in the methane feed stream to acetylene through pyrolysis and to emit an effluent stream including the acetylene;

a hydrocarbon conversion zone in communication with the supersonic reactor and configured to receive the effluent stream and convert at least a portion of the acetylene therein to another hydrocarbon compound in a product stream;

a hydrocarbon stream line for transporting the methane feed stream, the reactor effluent stream, and the product stream; and

a contaminant removal zone in communication with the hydrocarbon stream line for removing hydrides of arsenic, phosphorus, antimony, silicon, and boron from one of the methane feed stream, the effluent stream, and the product stream.


2
4
6
8
10
12
14
16
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
36

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2013/053541

A. CLASSIFICATION OF SUBJECT MATTER

(see extra sheet)

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)

C10G 9/00, C07C 7/12, 11/24, 2/76, 7/13, B01J 19/10

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)

Esp@cenet, USPTO DB, EAPATIS, Information retrieval system of FIPS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4724272 A (ROCKWELL INTERNATIONAL CORPORATION) 09.02.1988, claims, col. 5-6	1-10
Y	US 6960700 B1 (UOP LLC) 01.11.2005, col. 3, line 60 - col. 4, line 34	1-10
Y	EP 0263259 A2 (HUELS CHEMISCHE WERKE AG) 13.04.1988, abstract	7
A	US 5427689 A (PHILLIPS PETROLEUM COMPANY) 27.06.1995	1-10
A	US 6960700 B1 (RUSTAM H. SETHNA) 01.11.2005	1-10

☐ 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 document but published on or after the international filing date

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
05 November 2013 (05.11.2013)	23 January 2014 (23.01.2014)

Name and mailing address of the ISA/ FIPS
Russia, 123995, Moscow, G-59, GSP-5,
Berezhkovskaya nab., 30-1

Facsimile No. +7 (499) 243-33-37

Authorized officer

A. Sedov

Telephone No. (495)531-64-81

INTERNATIONAL SEARCH REPORT Classification of subject matter	International application No. PCT/US 2013/053541

C10G 9/00 *(2006.01)*
C07C 11/24 *(2006.01)*
C07C 2/76 *(2006.01)*
C07C 7/12 *(2006.01)*
B01J 19/10 *(2006.01)*