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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 May 2018 (11.05.2018)

WIPO | PCT

(10) International Publication Number
WO 2018/085076 A1

(51) International Patent Classification:
B01D 53/00 (2006.01) ***C10L 3/06*** (2006.01)
B01D 53/047 (2006.01) ***C10G 5/02*** (2006.01)
C07C 7/13 (2006.01) ***F25J 3/06*** (2006.01)

(21) International Application Number:
PCT/US2017/058003

(22) International Filing Date:
24 October 2017 (24.10.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/417,495 04 November 2016 (04.11.2016) US

(71) Applicant: **DOW GLOBAL TECHNOLOGIES LLC** [US/US]; 2040 Dow Center, Midland, MI 48674 (US).

(72) Inventors: **DUGAS, Ross, E.**; 2301 N. Brazosport Blvd, Freeport, TX 77541 (US). **BADHWAR, Ajay, N.**; 1254 Enclave Parkway, Houston, TX 77077 (US). **DANDEKAR, Preshit**; 6520 23rd Ave NE #203, Seattle, WA 98115 (US). **OLIVEROS PATINO, German, A.**; 2301 N. Brazosport Blvd, Freeport, TX 77541 (US).

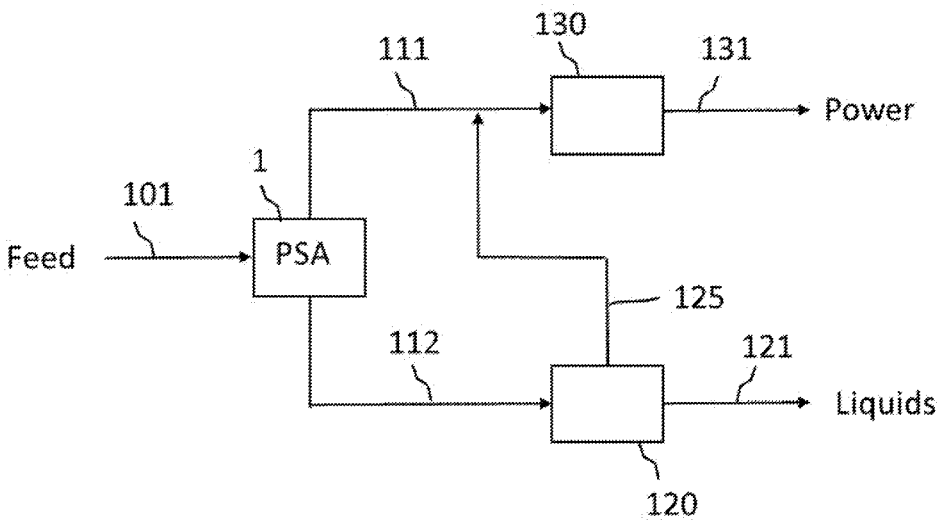
(74) Agent: **CHRISTY, M., Robert**; The Dow Chemical Company, Intellectual Property, P.O. Box 1967, Midland, MI 48641-1967 (US).

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

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH,

(54) Title: PSA PRODUCED HYDROCARBON GAS SUPPLY FOR POWER GENERATION

FIG. 3



(57) Abstract: The present invention relates to a method for running natural gas powered combustion systems, such as an internal combustion engine, a furnace, a fired heater, a power plant, an incinerator, and the like. In one embodiment of the present method, heavier hydrocarbons are separated from a natural gas feedstream in a PSA unit to provide the light hydrocarbon gas stream which is combined with an ethane plus tail gas stream from a liquefaction unit to fuel the combustion system. This method eliminates flaring any gas and minimizes the size requirements for the PSA unit.

WO 2018/085076 A1

[Continued on next page]

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

Published:

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

PSA PRODUCED HYDROCARBON GAS SUPPLY FOR POWER GENERATION

FIELD OF THE INVENTION

This invention relates to a method of improving the efficiency of a pressure swing adsorption process used to separate a natural gas stream into a light hydrocarbon stream and a heavy hydrocarbon streams wherein the light hydrocarbon stream may be used for running natural gas powered stationary combustion systems, for example, internal combustion engines, furnaces, fired heaters, power plants, or incinerators.

BACKGROUND OF THE INVENTION

Natural gas consists primarily of saturated hydrocarbon components such as methane, ethane, propane, butane, and heavier hydrocarbons. Natural gas typically contains about 60-100 mole percent methane, the balance being primarily heavier alkanes. Alkanes of increasing carbon number are normally present in decreasing amounts. Carbon dioxide, hydrogen sulfide, nitrogen, and other gases may also be present.

There are many reasons to separate the higher alkanes known as natural gas liquids (NGL) or heavier hydrocarbons from natural gas to provide a light hydrocarbon natural gas stream which is methane rich. For example, it is financially desirable to recover natural gas liquids from natural gas. NGLs including ethane, propane, butane, and lesser amounts of other heavy hydrocarbons may be used as petrochemical feedstocks where they have a higher value as compared to their value as a fuel gas component.

Another reason is to meet pipeline specifications or liquefied natural gas (LNG) specification for heating value, dew point, and condensation.

Moreover, oilfields are often located in remote locations where power grids have not yet been developed and electrical power is not available. Typically, fuels, such as diesel, to run onsite oilfield equipment need to be transported to such remote locations. While natural gas is often readily available in such remote locations, the use of raw gas is not feasible unless the natural gas liquids have first been removed. Natural gas containing NGLs have elevated BTU levels and are not be suitable for gas combustion systems that are designed to operate within a narrow BTU range. Using a natural gas with too high of BTU level may require higher maintenance costs, higher operating temperatures, reduced

equipment life expectancy, decreased power reduction, and/or generate increased pollution if operated at higher BTUs.

In addition to on-site equipment, equipment associated with the natural gas pipeline (i.e., engines used to pressurize the pipeline) may use raw natural gas as their primary fuel.

The present invention relates to an improved method of separating light and heavy hydrocarbon streams from a natural gas stream by adsorption onto a solid adsorbent with regeneration of the adsorbent at intervals using a pressure swing adsorption (PSA) process wherein the light hydrocarbon stream may be used to power onsite combustion equipment.

In a conventional PSA process a natural gas stream is fed in contact with a solid adsorbent to adsorb NGLs which gradually builds-up in the adsorbent while letting the lighter hydrocarbons pass through the system. The concentration of the heavier hydrocarbons in the adsorbent will gradually rise. The concentration of the heavier hydrocarbons in the adsorbent will not be uniform but will be highest at the upstream end of the adsorbent bed and will tail off progressively through a mass transfer zone in the adsorbent. If the process is conducted indefinitely, the mass transfer zone will progressively move downstream in the adsorbent bed until the component which is to be removed breaks through from the downstream end of the bed. Before this occurs, it is necessary to regenerate the adsorbent.

The adsorbent regeneration is done by stopping the flow of the natural gas to be treated, depressurising the adsorbent and, passing through the bed counter-current to the product feed direction a flow a purge stream, such as the produced lighter hydrocarbon stream, usually at a lower pressure than the natural gas to be treated and low in its content of the NGLs adsorbed on the bed. In PSA it is usual to use at least two adsorbent beds, with one being on-line while the other is regenerated. The depressurisation and regeneration of one bed may take place during the short time for which the other bed is on-line.

Sometimes, the resulting heavy hydrocarbon stream is passed through a liquefaction unit where some of the NGLs are condensed, optionally separated, and discharged either as a liquid phase mixture of NGLs or individual fractions of ethane, propane, butane, pentane, and/or heavier hydrocarbons (ethane plus). The components that are not liquefied are either flared or recycled back to the adsorption process. However, flaring gas may have a significant negative impact on the environment,

accounting for a significant amount of CO_2 and heat that is injected into the atmosphere. Alternatively, recycling the non-liquefied ethane plus hydrocarbons gas back to the PSA unit can cause increased load on the PSA unit due to the increased quantity of NGLs, especially impacted by the accumulation of species like ethane that may readily adsorb but do not sufficiently condense. This results in a need for a larger PSA unit and/or loss of separation efficiency.

It would be desirable to have a PSA process with improved efficiency to provide an onsite gas source to drive natural gas powered equipment at, or near wellheads, or associated with pipelines, especially in remote locations.

SUMMARY OF THE INVENTION

The present invention is a method to run a combustion system fueled by a hydrocarbon gas stream wherein the hydrocarbon gas stream is derived from a natural gas feedstream comprising methane and one or more of the natural gas liquids (NGLs): ethane, propane, butane, pentane, or heavier hydrocarbons, wherein some or all of the NGLs are separated from the natural gas feedstream by means of a pressure swing adsorbent (PSA) unit comprising the steps: (i) providing a natural gas feedstream to the PSA unit comprising an adsorption media, (ii) separating the natural gas feed stream in the PSA unit into a light hydrocarbon stream and a heavy hydrocarbon stream; (iii) passing the heavy hydrocarbon stream from the PSA unit to a liquefaction means to produce a liquid hydrocarbons stream and a non-liquefied ethane plus tail gas stream; (iv) recovering the liquid hydrocarbon stream as a mixture of hydrocarbons and/or further separating it into one or more individual liquid hydrocarbon streams; (v) combining the light hydrocarbon stream with the non-liquefied ethane plus tail gas stream to form a hydrocarbon gas stream; and (vi) providing the hydrocarbon gas stream to power a combustion system.

The method described herein above wherein the adsorption media is silica gel, alumina, silica-alumina, a zeolite, an activated carbon, a polymer supported silver chloride, a copper-containing resin, a porous cross-linked polymeric adsorbent, a pyrolized macroporous polymer, or mixtures thereof.

The method described herein above wherein the combustion system is an internal combustion engine, a furnace, a fired heater, a power plant, or an incinerator and the

natural gas feedstream is from an oil well, a gas well, a condensate well, or a natural gas pipeline, preferably an internal combustion engine used to power onsite equipment used for oilfield operations and/or to power equipment used to maintain and operate natural gas pipelines wherein the source of the natural gas feedstream is from an oil well, a gas well, a condensate well or to incorporate power production to a power grid.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic of a pressure swing adsorption (PSA) process.

FIG. 2 is a schematic of a conventional pressure swing adsorption (PSA) process.

FIG. 3 is a schematic of a pressure swing adsorption (PSA) process according to the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Raw natural gas comes from three types of wells: oil wells, gas wells, and condensate wells. Natural gas that comes from oil wells is typically termed “associated gas”. This gas can exist separate from oil in the formation (free gas), or dissolved in the crude oil (dissolved gas). Natural gas from gas and condensate wells, in which there is little or no crude oil, is termed “non-associated gas”. Gas wells typically produce raw natural gas by itself, while condensate wells produce free natural gas along with a semi-liquid hydrocarbon condensate. Whatever the source of the natural gas, once separated from crude oil (if present) it commonly exists as methane in mixtures with other hydrocarbons; principally ethane, propane, butane, and pentanes and to a lesser extent heavier hydrocarbons.

Raw natural gas often contain a significant amount of impurities, such as water or acid gases, for example carbon dioxide (CO_2), hydrogen sulfide (H_2S), sulfur dioxide (SO_2), carbon disulfide (CS_2), hydrogen cyanide (HCN), carbonyl sulfide (COS), or mercaptans as impurities. The term “natural gas feedstream” as used in the method of the present invention includes any natural gas source, raw or raw natural gas that has been treated one or more times to remove water and/or other impurities.

The terms "natural gas liquids" (NGL) and "ethane plus" (C_2+) and “heavier hydrocarbons” refer broadly to hydrocarbons having two or more carbons such as ethane,

propane, butane, and possibly small quantities of pentanes or heavier hydrocarbons. Preferably, NGL have a methane concentration of 5 mol percent or less.

The term "light hydrocarbon stream" or "methane rich" refers broadly to any vapor or liquid stream, e.g., after fractionation from which at least some ethane plus amounts have been recovered. Thus, a light hydrocarbon stream has a higher concentration of C_1 than the concentration of C_1 in associated and non-associated natural gas. Preferably, the concentration increase of C_1 is from removal of at least 80 mole percent of the targeted heavy hydrocarbons, which may vary by application.

One embodiment of the present invention is a method for running natural gas powered combustion systems, examples include, but are not limited to, an internal combustion engine, a furnace, a fired heater, a power plant, an incinerator, and the like, using a methane-rich natural gas supply having reduced heavier hydrocarbons content.

Preferably, the present invention is a method to run an internal combustion engine, preferably an internal combustion engine used to power onsite equipment used for oilfield operations as well as equipment associated with the natural gas pipeline, for example compressors, generators, pumps, condensers, chillers, surge vessels, separation tanks, heat exchangers, additional PSA systems, etc.

The source of the natural gas feedstream useful for the method of the present invention can be an oil well, a gas well, a condensate well, or a natural gas pipeline.

It is advantageous to remove the heavier hydrocarbons from the natural gas feedstream prior to combustion to capture value for them. This approach may also eliminate the need to transport fuels to, or otherwise provide means to power, the engines in remote areas thus reducing transportation costs as well as truck traffic. Such a methane-rich natural gas supply may reduce emissions, especially compared to diesel fueled equipment and/or natural gas supply containing higher hydrocarbons having higher energy ratings. Further, such a gas supply may reduce wear on equipment, for example reducing or eliminating knocking, which can result in reducing maintenance costs and/or improving equipment life expectancy.

Preferably, the hydrocarbon gas stream of the method of the present invention has a lower heating value (LHV) of in BTU/Sft^3 equal to or less than 1200, more preferably equal to or less than 1150, more preferably equal to or less than 1100, and most preferably a BTU value of equal to or less than 1050.

Another embodiment of the present invention is providing a more efficient PSA process to separate light hydrocarbons from heavy hydrocarbons. In the process of the present invention, the adsorption/desorption separation process of a feed natural gas stream comprising NGLs to a heavy hydrocarbon stream and a light hydrocarbon stream is performed within a pressure swing adsorption (PSA) unit comprising one or more vessel containing an adsorbent material. The separation step is followed by an adsorbent regeneration sequence comprising the steps of depressurizing/venting the adsorption vessel down to low pressure followed by purging the adsorbent-containing vessel with a gas stream, typically the light hydrocarbon gas stream, and repressurizing the adsorbent-containing vessel with the feed gas back to the pressure level at which the gas stream was initially contacted with the adsorbent.

Also preferably, the depressurization is partly performed via one or more pressure equalization steps with other PSA vessels undergoing said repressurizing, **FIG. 1**.

In one type of PSA, the depressurizing is performed down to vacuum pressure levels by connecting the adsorption vessel to a vacuum pump (i.e. vacuum swing adsorption or VSA). The skilled practitioner will appreciate that this will improve the adsorbent's rejection of the adsorbed impurities during the depressurization step, albeit at the expense of power.

Also preferably, the adsorbent is purged or rinsed with a portion of the light hydrocarbon gas stream subsequent to said depressurization step and prior to said repressurization step. The skilled practitioner will appreciate that this will further improve the adsorbent's rejection of the adsorbed NGLs, albeit at the expense of methane recovery. Note however that in a typical PSA process, the purge step is performed at 1 atm pressure. By lowering the purge pressure to 0.1 atm, one may obtain the same degree of purging with about 10% of the gas required at 1 atm.

FIG. 1 depicts a continuous PSA process **1**. The first step, the adsorption step, in the continuous process is to feed a natural gas mixture comprising methane and heavier hydrocarbons, or feed gas, which is compressed to a pressure, preferably between 4-40 bar, through line **101** into line **3** with valves **11**, **13**, **31**, **24**, and **22** open and valves **12**, **14**, **23**, and **21** closed. The pressurized gaseous mixture comprising methane flows through line **3** passes through open valve **11** into the first vessel **10** at a first pressure P_1 where it contacts the adsorbent and the heavier hydrocarbons are adsorbed. The methane rich

gaseous mixture, or light hydrocarbons, flows from the top of the vessel **10** into line **4** through valve **13** and exits through line **111** with a pressure drop.

A portion of the light hydrocarbon stream leaving the top of vessel **10** is used as purge gas to regenerate the adsorbent in a second vessel **20**. The purge gas flows through lines **6** and **7** and open valves **31** and **24** into the top of vessel **20** which is at a second pressure P_2', where P_2' is less than P_1. The adsorption of heavier hydrocarbons is reversible from the adsorbent media and the heavier hydrocarbons desorbs from the adsorbent in vessel **20** into the purge gas which passes out the bottom of vessel **20** through line **5**, open valve **22**, and out through line **112** as a heavy hydrocarbon stream comprising some methane, resulting in vessel **20** containing a regenerated adsorbent media.

After the adsorption step in vessel **10** is completed, the adsorbent in vessel **10** needs to be regenerated. In the second step of the continuous PSA process, vessel **10** will be depressurized and vessel **20** will be repressurized. During this step, valves **11**, **13**, **14**, **31**, **22**, **23**, and **24** are closed and valves **12** and **21** are open. The pressure P_1 in the first vessel **10** is lowered to P_1' (optionally to vacuum) by gas withdrawal through valve **12** to line **112**. The compressed feed gas is fed through line **101** into line **3** and valve **21** to repressurize vessel **20** from the low pressure P_2' to the high adsorption pressure P_2 (i.e., $P_2 > P_2'$).

In the third step of the continuous PSA process, valves **11**, **13**, **24**, and **22** remain closed and valves **12** and **21** remain open but valves **14**, **31**, and **23** are opened. The compressed feed gas is fed through line **101** into line **3** with valves **21**, **23**, **31**, **14**, and **12** open and valves **11**, **13**, **24**, and **22** closed. The pressurized gaseous mixture comprising methane and heavier hydrocarbons flows through line **3** passes through open valve **21** into the second vessel **20** at the pressure P_2 where it contacts the regenerated adsorbent media. The light hydrocarbon stream, or methane rich gaseous mixture, flows from the top of the vessel **20** into line **4** through valve **23** and exits through line **111** with a pressure drop.

A portion of the light hydrocarbon stream leaving the top of vessel **20** is used as purge gas to regenerate the adsorbent in the first vessel **10**. The purge gas flows through line **6** and **7** and open valves **14** and **31** into the top of vessel **10** which is at a second pressure P_1', where P_1' is less than P_2. The heavier hydrocarbons desorb from the adsorbent in vessel **10** into the purge gas, forming a loaded purge gas which passes out the bottom of vessel **10** through line **5**, open valve **12**, and out through line **112** as a heavy

hydrocarbon stream comprising some methane, resulting in vessel **10** containing a regenerated adsorbent media.

After the adsorption step in vessel **20** is completed, the adsorbent in vessel **20** needs to be regenerated. In the fourth step of the continuous PSA cycle, vessel **20** is depressurized and vessel **10** is repressurized. During this step, valves **21**, **23**, **24**, **31**, **12**, **13**, and **14** are closed and valves **11** and **22** are open. The pressure P_2 in vessel **20** is lowered to P_2' (optionally to vacuum) by gas withdrawal through valve **22** to line **112**. The compressed feed gas is fed through line **101** into line **3** and valve **11** to repressurize vessel **10** from the low pressure P_1' to the high adsorption pressure P_1 (i.e., $P_1 > P_1'$). When vessel **10** pressure reaches P_1, the PSA process will go to next cycle beginning with the first step.

Although a particular embodiment of a PSA process is disclosed in **FIG. 1** for illustrative purposes, it will be recognized that variations or modifications of the disclosed process lie within the scope of the present invention. For example, in another embodiment, there may be multiple adsorbent vessels, columns, or beds and/or the adsorbent vessel(s), column(s), or bed(s) may be regenerated in-place as exemplified by USP 3,458,973, which is incorporated herein by reference in its entirety. In other embodiments, PSA cycles may incorporate one or more of pressure equalization, reflux, and/or other strategies to improve performance, in some industrial PSA cycles there may be 8 steps, in some cases 12 steps or more.

Suitable adsorbents are solids having a microscopic structure. The internal surface of such adsorbents is preferably between 100 to 2000 m^2/g, more preferably between 500 to 1500 m^2/g, and even more preferably 1000 to 1300 m^2/g. The nature of the internal surface of the adsorbent in the adsorbent bed is such that C_2 and heavier hydrocarbons are adsorbed. Suitable adsorbent media include materials based on silica, silica gel, alumina or silica-alumina, zeolites, activated carbon, polymer supported silver chloride, copper-containing resins. Most preferred adsorbent media is a porous cross-linked polymeric adsorbent or a partially pyrolized macroporous polymer. Preferably, the internal surface of the adsorbent is non-polar.

In one embodiment, the present invention is the use of an adsorbent media to separate NGLs from a natural gas stream. The mechanism by which the macroporous polymeric adsorbent separates the NGLs from the natural gas stream is a combination of adsorption and absorption; the dominating mechanism at least is believed to be adsorption.

Accordingly, the terms "adsorption" and "adsorbent" are used throughout this specification, although this is done primarily for convenience. The invention is not considered to be limited to any particular mechanism.

When an adsorbent media has adsorbed any amount of ethane plus (C_2+) hydrocarbons it is referred to as "loaded". Loaded includes a range of adsorbance from a low level of hydrocarbons up to and including saturation with adsorbed hydrocarbons.

The term "macroporous" is used in the art interchangeably with "macroreticular," and refers in general to pores with diameters of about 500 Å or greater. "Mesopores" are characterized as pores of between 50 Å and larger but less than 500 Å. "Micropores" are characterized as pores of less than 50 Å. The engineered distribution of these types of pores gives rise to the desired properties of high adsorption capacity for NGLs and ease of desorption of NGLs under convenient/practical chemical engineering process modifications (increase in temperature or reduced pressure [vacuum]). The process giving rise to the distribution of micropores, mesopores and macropores can be achieved in various ways, including forming the polymer in the presence of an inert diluent or other porogen to cause phase separation and formation of micropores by post cross-linking.

In one embodiment, the adsorbent media of the present invention is a macroporous polymeric adsorbent of the present invention is a post cross-linked polymeric synthetic adsorbents engineered to have high surface area, high pore volume and high adsorption capacities as well as an engineered distribution of macropores, mesopores and micropores.

Preferably, the macroporous polymeric adsorbent of the present invention is hypercrosslinked and/or methylene bridged having the following characteristics: a BET surface area of equal to or greater than 500 m^2/g and preferably equal to or greater than 1,000 m^2/g, and having a particle size of 300 microns to 1500 microns, preferably 500 to 1200 microns.

Examples of monomers that can be polymerized to form macroporous polymeric adsorbents useful are styrene, alkylstyrenes, halostyrenes, haloalkylstyrenes, vinylphenols, vinylbenzyl alcohols, vinylbenzyl halides, and vinylnaphthalenes. Included among the substituted styrenes are ortho-, meta-, and para-substituted compounds. Specific examples are styrene, vinyltoluene, ethylstyrene, t-butylstyrene, and vinyl benzyl chloride, including ortho-, meta-, and para-isomers of any such monomer whose molecular structure permits this type of isomerization. Further examples of monomers are polyfunctional compounds. One preferred class is polyvinylidene compounds, examples of which are divinylbenzene,

trivinylbenzene, ethylene glycol dimethacrylate, divinylsulfide and divinylpyridine. Preferred polyvinylidene compounds are di- and trivinyl aromatic compounds. Polyfunctional compounds can also be used as crosslinkers for the monomers of the first group.

One preferred method of preparing the polymeric adsorbent is by swelling the polymer with a swelling agent, then crosslinking the polymer in the swollen state, either as the sole crosslinking reaction or as in addition to crosslinking performed prior to swelling. When a swelling agent is used, any pre-swelling crosslinking reaction will be performed with sufficient crosslinker to cause the polymer to swell when contacted with the swelling agent rather than to dissolve in the agent. The degree of crosslinking, regardless of the stage at which it is performed, will also affect the porosity of the polymer, and can be varied to achieve a particular porosity. Given these variations, the proportion of crosslinker can vary widely, and the invention is not restricted to particular ranges. Accordingly, the crosslinker can range from about 0.25% of the polymer to about 45%. Best results are generally obtained with about 0.75% to about 8% crosslinker relative to the polymer, the remaining (noncrosslinking) monomer constituting from about 92% to about 99.25% (all percentages are by weight).

Other macroporous polymeric adsorbents useful in the practice of this invention are copolymers of one or more monoaromatic monomers with one or more nonaromatic monovinylidene monomers. Examples of the latter are methyl acrylate, methyl methacrylate and methylethyl acrylate. When present, these nonaromatic monomers preferably constitute less than about 30% by weight of the copolymer.

The macroporous polymeric adsorbent is prepared by conventional techniques, examples of which are disclosed in various United States patents. Examples are USP 4,297,220; 4,382,124; 4,564,644; 5,079,274; 5,288,307; 4,950,332; and 4,965,083. The disclosures of each of these patents are incorporated herein by reference in their entirety.

For polymers that are swollen and then crosslinked in the swollen state, the crosslinking subsequent to swelling can be achieved in a variety of ways, which are further disclosed in the patents cited above. One method is to first haloalkylate the polymer, then swell it and crosslink by reacting the haloalkyl moieties with aromatic groups on neighboring chains to form an alkyl bridge. Haloalkylation is achieved by conventional means, an example of which is to first swell the polymer under non-reactive conditions with the haloalkylating agent while including a Friedel-Crafts catalyst dissolved in the

haloalkylating agent. Once the polymer is swollen, the temperature is raised to a reactive level and maintained until the desired degree of haloalkylation has occurred. Examples of haloalkylating agents are chloromethyl methyl ether, bromomethyl methyl ether, and a mixture of formaldehyde and hydrochloric acid. After haloalkylation, the polymer is swelled further by contact with an inert swelling agent. Examples are dichloroethane, chlorobenzene, dichlorobenzene, ethylene dichloride, methylene chloride, propylene dichloride, and nitrobenzene. A Friedel-Crafts catalyst can be dissolved in the swelling agent as well, since the catalyst will be used in the subsequent crosslinking reaction. The temperature is then raised to a level ranging from about 60°C to about 85°C in the presence of the catalyst, and the bridging reaction proceeds. Once the bridging reaction is complete, the swelling agent is removed by solvent extraction, washing, drying, or a combination of these procedures.

The pore size distribution and related properties of the finished adsorbent can vary widely and no particular ranges are critical to the invention. In most applications, best results will be obtained at a porosity (total pore volume) within the range of from about 0.5 to about 1.5 cc/g of the polymer. A preferred range is about 0.7 to about 1.3 cc/g. Within these ranges, the amount contributed by macropores (i.e., pores having diameters of 500 Å or greater) will preferably range from about 0.025 to about 0.6 cc/g, and most preferably from about 0.04 to about 0.5 cc/g. The surface area of the polymer, as measured by nitrogen adsorption methods such as the well-known BET method, will in most applications be within the range of about 150 to about 2100 m^2/g, and preferably from about 400 to about 1400 m^2/g. The average pore diameter will most often range from about 10 Å to about 100 Å.

The form of the macroporous polymeric adsorbent is likewise not critical and can be any form which is capable of containment and contact with a flowing compressed air stream. Granular particles and beads are preferred, ranging in size from about 50 to about 5,000 microns, with a range of about 500 to about 3,000 microns particularly preferred. Contact with the adsorbent can be achieved by conventional flow configurations of the gas, such as those typically used in fluidized beds or packed beds. The adsorbent can also be enclosed in a cartridge for easy removal and replacement and a more controlled gas flow path such as radial flow.

The macroporous polymeric adsorbent can function effectively under a wide range of operating conditions. The temperature will preferably be within any range which does

not cause further condensation of vapors or any change in physical or chemical form of the adsorbent. Preferred operating temperatures are within the range of from 5°C to 75°C, and most preferably from 10°C to 50°C. In general, operation at ambient temperature or between -30°C below ambient temperature to15°C above ambient will provide satisfactory results. The pressure of the natural gas stream entering the adsorbent bed can vary widely as well, preferably extending from 2 psig (115 kPa) to 1000 psig (7000 kPa). The pressure will generally be dictated by the plant unit where the product gas will be used. A typical pressure range is from 100 psig (795 kPa) to 500 psig (3549 kPa). The residence time of the natural gas stream in the adsorbent bed will most often range from 10 second to 300 seconds, and preferably from 30 second to 200 seconds. The space velocity of the natural gas stream through the bed will most often fall within the range of 0.05 foot per second to 2 feet per second, with a range of 0.1 foot per second to 1 foot per second preferred. Finally, the relative humidity can have any value up to 100%.

The macroporous polymeric adsorbents of the present invention described herein above can be used to separate ethane, propane, butane, pentane, and heaver hydrocarbons from mixed gases containing methane. Preferably, the macroporous polymeric adsorbents of the present invention adsorb equal to or greater than 60 cm^3 STP of propane per gram of sorbent at 35°C and 500 mmHg of propane. Preferably, the adsorbents of the present invention adsorb equal to or greater than 60 cm^3 STP of n-butane per gram of sorbent at 35°C and 100 mmHg of n-butane. Furthermore, these materials are able to be degassed of propane or n-butane and then able to readsorb equal to or greater than 60 cm^3 STP of propane per gram of sorbent at 35°C and 500 mmHg of propane or readsorb greater than 60 cm^3 STP of n-butane per gram of sorbent at 35°C and 100 mmHg of n-butane at least once. Preferably, the adsorbents of the present invention adsorb equal to or greater than 30 cm^3 STP of ethane per gram of sorbent at 35°C and 600 mmHg of ethane. Preferably, the adsorbents of the present invention adsorb equal to or greater than 100 cm^3 STP of pentane per gram of sorbent at 35°C and 50 mmHg of pentane.

In another embodiment, the adsorbent media of the present invention is a pyrolized macroporous polymeric adsorbent media to extract NGLs from a natural gas stream.

Pyrolized macroporous polymeric adsorbent media are well known, for instance see USP 4,040,990, incorporated by reference herein in its entirety. Partially pyrolyzed particles, preferably in the form of beads or spheres, produced by the controlled decomposition of a synthetic polymer of specific initial porosity. In a preferred

embodiment, the pyrolyzed particles are derived from the thermal decomposition of macroreticular ion exchange resins containing a macroporous structure.

In general pyrolysis comprises subjecting the starting polymer to controlled temperatures for controlled periods of time under certain ambient conditions. The primary purpose of pyrolysis is thermal degradation while efficiently removing the volatile products produced.

The maximum temperatures may range from about 300°C to up to about 900°C, depending on the polymer to be treated and the desired composition of the final pyrolyzed particles. Higher temperature, e.g., about 700°C and higher result in extensive degradation of the polymer with the formation of molecular sieve sized pores in the product.

Most desirably, thermal decomposition (alternatively denoted "pyrolysis" or "heat treatment") is conducted in an inert atmosphere comprised of, for example, argon, neon, helium, nitrogen, or the like, using beads of macroreticular synthetic polymer substituted with a carbon-fixing moiety which permits the polymer to char without fusing in order to retain the macroreticular structure and give a high yield of carbon. Among the suitable carbon-fixing moieties are sulfonate, carboxyl, amine, halogen, oxygen, sulfonate salts, carboxylate salts and quaternary amine salts. These groups are introduced into the starting polymer by well-known conventional techniques, such as those reactions used to functionalize polymers for production of ion exchange resins. Carbon-fixing moieties may also be produced by imbibing a reactive precursor thereof into the pores of macroreticular polymer which thereupon, or during heating, chemically binds carbon-fixing moieties onto the polymer. Examples of these latter reactive precursors include sulfuric acid, oxidizing agents, nitric acid, Lewis acids, acrylic acid, and the like.

Suitable temperatures for practicing the process of this invention are generally within the range of 300°C to about 900°C, although higher temperatures may be suitable depending upon the polymer to be treated and the desired composition of the final pyrolyzed product. At temperatures above about 700°C the starting polymer degrades extensively with the formation of molecular sieve sized pores in the product, i.e., 4 Å to 6 Å average critical dimension, yielding a preferred class of adsorbents according to this invention. At lower temperatures, the thermally-formed pores usually range from 6 Å to as high as 50 Å in average critical size. A preferred range of pyrolysis temperatures is between about 400°C and 800°C. As will be explained more fully hereinafter,

temperature control is essential to yield a partially pyrolyzed material having the composition, surface area, pore structures and other physical characteristics of the desired product. The duration of thermal treatment is relatively unimportant, providing a minimum exposure time to the elevated temperature is allowed.

A wide range of pyrolyzed resins may be produced by varying the porosity and/or chemical composition of the starting polymer and also by varying the conditions of thermal decomposition. In general, the pyrolyzed resins of the invention have a carbon to hydrogen ratio of 1.5 : 1 to 20 : 1, preferably 2.0 : 1 to 10 : 1, whereas activated carbon normally has a C/H ratio much higher, at least greater than 30 : 1 (Carbon and Graphite Handbook, Charles L. Mantell, Interscience Publishers, N.Y. 1968, p. 198). The product particles contain at least 85% by weight of carbon with the remainder being principally hydrogen, alkali metals, alkaline earth metals, nitrogen, oxygen, sulfur, chlorine, etc., derived from the polymer or the functional group (carbon-fixing moiety) contained thereon and hydrogen, oxygen, sulfur, nitrogen, alkali metals, transition metals, alkaline earth metals and other elements introduced into the polymer pores as components of a filler (may serve as a catalyst and/or carbon-fixing moiety or have some other functional purpose).

The pore structure of the final product must contain at least two distinct sets of pores of differing average size, i.e., multimodal pore distribution. The larger pores originate from the macroporous resinous starting material which preferably contain macropores ranging from between 50 Å to 100,000 Å in average critical dimension. The smaller pores, as mentioned previously, generally range in size from 4 Å to 50 Å, depending largely upon the maximum temperature during pyrolysis. Such multimodal pore distribution is considered a novel and essential characteristic of the composition of the invention.

The pyrolyzed polymers of the invention have relatively large surface area resulting from the macroporosity of the starting material and the smaller pores developed during pyrolysis. In general the overall surface area as measured by nitrogen adsorption ranges between about 50 and 1500 m^2/gram. Of this, the macropores will normally contribute 6 to 700 m^2/gram, preferably 6 to 200 m^2/g, as calculated by mercury intrusion techniques, with the remainder contributed by the thermal treatment. Pore-free polymers, such as "gel" type resins which have been subjected to thermal treatment in the prior art do

not contribute the large pores essential to the adsorbents of the invention nor do they perform with the efficiency of the pyrolyzed polymers described herein.

The duration of pyrolysis depends upon the time needed to remove the volatiles from the particular polymer and the heat transfer characteristics of the method selected. In general, the pyrolysis is very rapid when the heat transfer is rapid, e.g., in an oven where a shallow bed of material is pyrolyzed, or in a fluidized bed. To prevent burning of the pyrolyzed polymer, normally the temperature of the polymer is reduced to not more than 400°C, preferably not more than 300°C, before the pyrolyzed material is exposed to air. The most desirable method of operation involves rapid heating to the maximum temperature, holding the temperature at the maximum for a short period of time (in the order of 0 to 20 minutes) and thereafter quickly reducing the temperature to room temperature before exposing the sample to air. Products according to the invention have been produced by this preferred method by heating to 800°C and cooling in a period of 20 to 30 minutes. Longer holding periods at the elevated temperatures are also satisfactory, since no additional decomposition appears to occur unless the temperature is increased.

Activating gases such as CO_2, NH_3, O_2, H_2O or combinations thereof in small amounts tend to react with the polymer during pyrolysis and thereby increase the surface area of the final material. Such gases are optional and may be used to obtain special characteristics of the adsorbents.

The starting polymers which may be used to produce the pyrolyzed resins of the invention include macroreticular homopolymers or copolymers of one or more monoethylenically or polyethylenically unsaturated monomers or monomers which may be reacted by condensation to yield macroreticular polymers and copolymers. The macroreticular resins used as precursors in the formation of macroreticular heat treated polymers are not claimed as new compositions of matter in themselves. Any of the known materials of this type with an appropriate carbon-fixing moiety is suitable. The preferred monomers are those aliphatic and aromatic materials which are ethylenically unsaturated.

Examples of suitable monoethylenically unsaturated monomers that may be used in making the granular macroreticular resin include: esters of acrylic and methacrylic acid such as methyl, ethyl, 2-chloro ethyl, propyl, isobutyl, isopropyl, butyl, tert-butyl, sec-butyl, ethylhexyl, amyl, hexyl, octyl, decyl, dodecyl, cyclohexyl, isobornyl, benzyl, phenyl, alkylphenyl, ethoxymethyl, ethoxyethyl, ethoxypropyl, propoxymethyl, propoxyethyl, propoxypropyl, ethoxyphenyl, ethoxybenzyl, ethoxycyclohexul,

hydroxyethyl, hydroxypropyl, ethylene, propylene, isobutylene, diisobutylene, styrene, ethylvinylbenzene, vinyltoluene, vinylbenzylchloride, vinyl chloride, vinyl acetate, vinylidene chloride, dicyclopentadiene, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, diacetone acrylamide, functional monomers such as vinylbenzene, sulfonic acid, vinyl esters, including vinyl acetate, vinyl propionate, vinyl butyrate, vinyl laurate, vinyl ketones including vinyl methyl ketone, vinyl ethyl ketone, vinyl isopropyl ketone, vinyl n-butyl ketone, vinyl hexyl ketone, vinyl octyl ketone, methyl isopropenyl ketone, vinyl aldehydes including acrolein, methacrolein, crotonaldehyde, vinyl ethers including vinyl methyl ether, vinyl ethyl ether, vinyl propyl ether, vinyl isobutyl ether, vinylidene compounds including vinylidene chloride bromide, or bromochloride, also the corresponding neutral or half-acid half-esters or free diacids of the unsaturated dicarboxylic acids including itaconic, citraconic, aconitic, fumaric, and maleic acids, substituted acrylamides, such as N-monoalkyl, -N,N-dialkyl-, and N-dialkylaminoalkylacrylamides or methacrylamides where the alkyl groups may have from one to eighteen carbon atoms, such as methyl, ethyl, isopropyl, butyl, hexyl, cyclohexyl, octyl, dodecyl, hexadecyl and octadecyl aminoalkyl esters of acrylic or methacrylic acid, such as .beta.-dimethylaminoethyl, .beta.-diethylaminoethyl or 6-dimethylaminohexyl acrylates and methacrylates, alkylthioethyl methacrylates and acrylates such as ethylthioethyl methacrylate, vinylpyridines, such as 2-vinylpyridine, 4-vinylpyridine, 2-methyl-5-vinylpyridine, and so on.

In the case of copolymers containing ethylthioethyl methacrylate, the products can be oxidized to, if desired, the corresponding sulfoxide or sulfone.

Polyethylenically unsaturated monomers which ordinarily act as though they have only one such unsaturated group, such as isoprene, butadiene, and chloroprene, may be used as part of the monoethylenically unsaturated category.

Examples of polyethylenically unsaturated compounds include: divinylbenzene, divinylpyridine, divinylnaphthalenes, diallyl phthalate, ethylene glycol diacrylate, ethylene glycol dimethacrylate, trimethylolpropanetrimethacrylate, divinylsulfone, polyvinyl or polyallyl ethers of glycol, of glycerol, of pentaerythritol, of diethyleneglycol, of monothio or dithio-derivatives of glycols, and of resorcinol, divinylketone, divinylsylfide, allyl acrylate, diallyl maleate, diallyl fumarate, diallyl succinate, diallyl carbonate, diallyl malonate, diallyl oxalate, diallyl adipate, diallyl sebacate, divinyl sebacate, diallyl tartrate, diallyl silicate, triallyl tricarballylate, triallyl aconitate, triallyl citrate, triallyl phosphate,

N,N'-methylenediacrylamide, N,N'-methylenedimethacrylamide, N,N'-ethylenediacrylamide, trivinylbenzene, trivinylnaphthalenes, and polyvinylanthracenes.

A preferred class of monomers of this type is aromatic ethylenically unsaturated molecules such as styrene, vinyl pyridine, vinyl naphthalene, vinyl toluene, phenyl acrylate, vinyl xylenes, and ethylvinylbenzene.

Examples of preferred polyethylenically unsaturated compounds include divinyl pyridine, divinyl naphthalene, divinylbenzene, trivinylbenzene, alkyldivinylbenzenes having from 1 to 4 alkyl groups of 1 to 2 carbon atoms substituted in the benzene nucleus, and alkyltrivinylbenzenes having 1 to 3 alkyl groups of 1 to 2 carbon atoms substituted in the benzene nucleus. Besides the homopolymers and copolymers of these poly(vinyl) benzene monomers, one or more of them may be copolymerized with up to 98% (by weight of the total monomer mixture) of (1) monoethylenically unsaturated monomers, or (2) polyethylenically unsaturated monomers other than the poly(vinyl)benzenes just defined, or (3) a mixture of (1) and (2). Examples of the alkyl-substituted di- and tri-vinyl-benzenes are the various vinyltoluenes, the divinylethylbenzene, 1,4-divinyl-2,3,5,6-tetramethylbenzene, 1,3,5-trivinyl-2,4,6-trimethylbenzene, 1,4-divinyl, 2,3,6-triethylbenzene, 1,2,4-trivinyl-3,5-diethylbenzene, 1,3,5-trivinyl-2-methylbenzene.

Most preferred are copolymers of styrene, divinylbenzene, and ethylvinylbenzene.

Examples of suitable condensation monomers include: (a) aliphatic dibasic acids such as maleic acid, fumaric acid, itaconic acid, 1,1-cyclobutanedicarboxylic acid, etc.; (b) aliphatic diamines such as piperazine, 2-methylpiperazine, cis, cis-bis (4-aminocyclohexyl) methane, metaxylylenediamine, etc.; (c) glycols such as diethylene glycol, triethylene glycol, 1,2-butanediol, neopentyl glycol etc.; (d) bischloroformates such as cis and trans- 1,4-cyclohexyl bischloroformate, 2,2,2,4-tetramethyl-1,3-cyclobutyl bischloroformate and bischloroformates of other glycols mentioned above, etc.; (e) hydroxy acids such as salicylic acid, m- and p-hydroxy-benzoic acid and lactones, derived therefrom such as the propiolactones, valerolactones, caprolactones, etc.; (f) diisocyanates such as cis and trans-cyclopropane-1,2 -diisocyanate, cis and trans-cyclobutane-1-2-diisocyanate etc.; (g) aromatic diacids and their derivatives (the esters, anhydrides and acid chlorides) such as phthalic acid, phthalic anhydride, terephthalic acid, isophthalic acid, dimethylphthalate, etc.; (h) aromatic diamines such as benzidine, 4,4'-methylenediamine, bis(4-aminophenyl) ether, etc.; (i) bisphenols such as bisphenol A, bisphenol C, bisphenol F, phenolphthalein, recorcinol, etc.; (j) bisphenol

bis(chloroformates) such as bisphenol A bis(chloroformate), 4,4' -dihydroxybenzophenone bis(chloroformate) etc.; (k) carbonyl and thiocarbonyl compounds such as formaldehyde, acetaldehyde, thioacetone acetone, etc.; (1) phenol and derivatives such as phenol, alkylphenols, etc.; (m) polyfunctional cross-linking agents such as tri or poly basic acids such as trimellitic acid, tri or polyols such as glycerol, tri or polyamines such as diethylenetriamine; and other condensation monomers and mixtures of the foregoing.

Ion exchange resins produced from aromatic and/or aliphatic monomers provide a preferred class of starting polymers for production of porous adsorbents. The ion exchange resin may also contain a functional group selected from cation, anion, strong base, weak base, sulfonic acid, carboxylic acid, oxygen containing, halogen and mixtures of the same. Further, such ion exchange resins may optionally contain an oxidizing agent, a reactive substance, sulfuric acid, nitric acid, acrylic acid, or the like at least partially filling the macropores of the polymer before heat treatment.

The synthetic polymer may be impregnated with a filler such as carbon black, charcoal, bonechar, sawdust or other carbonaceous material prior to pyrolysis. Such fillers provide an economical source of carbon which may be added in amounts up to about 90% by weight of the polymer.

The starting polymers, when ion exchange resins, may optionally contain a variety of metals in their atomically dispersed form at the ionic sites. These metals may include iron, copper, silver, nickel, manganese, palladium, cobalt, titanium, zirconium, sodium, potassium, calcium, zinc, cadmium, ruthenium, uranium and rare earths such as lanthanum. By utilizing the ion exchange mechanism it is possible for the skilled technician to control the amount of metal that is to be incorporated as well as the distribution.

Although the incorporation of metals onto the resins is primarily to aid their ability to serve as catalytic agents, useful adsorbents may also contain metal.

Synthetic polymers, ion exchange resins whether in the acid, base or metal salt form are commercially available. According to the invention there is also provided an adsorption process for separating components from a gaseous or liquid medium which comprises contacting the medium with particles of a pyrolyzed synthetic polymer.

For example it has been discovered that a styrenedivinylbenzene based strongly acidic exchange resin pyrolyzed from any of the forms of Hydrogen, Iron (III), Copper (II), Silver (I) or Calcium (II) can decrease the concentration of vinylchloride in air

preferably dry air from initial concentration of 2 ppm to 300,000 ppm to a level of less than 1 ppm at flow rates of 1 bedvolume/minute to 600 bedvolume/minute preferably 10 to 200 bedvolume/minute.

The partially pyrolyzed macroporous polymer adsorbent of the present invention disclosed herein above are able to adsorb greater than 25 cm^3 STP of ethane per gram of sorbent at 35°C and 200 mmHg of ethane and greater than 30 cm^3 STP of propane per gram of sorbent at 35°C and 100 mmHg of propane. Furthermore, these materials are able to be degassed of ethane or propane and then able to readsorb greater than 25 cm^3 STP of ethane per gram of sorbent at 35°C and 200 mmHg of ethane, or readsorb greater than 30 cm^3 STP of propane per gram of sorbent at 35°C and 100 mmHg of propane one or more times.

Now referring to the figures. **FIG. 2** depicts a known process for treating a natural gas stream to separate a light hydrocarbons stream from a heavy hydrocarbons stream. The separation takes place in a pressure swing adsorption (PSA) unit **1**. The separation process comprises the steps of (a) passing a natural gas feedstream **101** through a PSA adsorption unit **1** comprising an adsorbent media which adsorbs heavier hydrocarbons (C_2, C_3, C_4, C_5, etc.) to obtain (i) a methane-rich or light hydrocarbon gas product **111** and (ii) a heavy hydrocarbons stream **112**. The adsorbent is regenerated in the PSA unit as discussed herein above. The light hydrocarbon stream **111** passes into an internal combustion engine **130** to produce power. The heavy hydrocarbon stream **112** is passed through a liquefaction means **120** which produces a liquid hydrocarbons stream **121** and a non-liquefied ethane plus tail gas stream **122** and/or **123**. Suitable liquefaction means may include, but is not limited to, mechanical refrigeration units (MRUs), lean oil absorption, distillation, Joule Thompson technology, or the like. The liquid hydrocarbon stream **121** may be recovered either as a mixture of hydrocarbons or may be further separated into one or more individual liquid hydrocarbon streams. The non-liquefied ethane plus tail gas stream is either flared **122** or recycled **123** back to the PSA unit.

Although a particular preferred embodiment of the invention is disclosed in **FIG. 3** for illustrative purposes, it will be recognized that variations or modifications of the disclosed process lie within the scope of the present invention. The improvement in the process of the present invention is that the non-liquefied ethane plus tail gas stream **125** is not flared or recycled back into the PSA unit **1**. In the process of the current invention, the natural gas feed stream is fed **101** into a PSA unit **1** wherein the separation of the light

hydrocarbon stream **111** from the heavy hydrocarbon stream **112** occurs. The separation process comprises the steps of (a) passing a natural gas feedstream **101** through a PSA adsorption unit **1** comprising an adsorbent media which adsorbs heavier hydrocarbons (C_2, C_3, C_4, C_5, etc.) to obtain (i) a methane-rich or light hydrocarbon gas product **111** and (ii) a heavy hydrocarbons stream **112**. The adsorbent is regenerated in the PSA unit as discussed herein above. The heavy hydrocarbon stream **112** is passed through a liquefaction means **120** which produces a liquid hydrocarbons stream **121** and a non-liquefied ethane plus tail gas stream **125**. The liquid hydrocarbon stream **121** may be recovered either as a mixture of hydrocarbons or may be further separated into one or more individual liquid hydrocarbon streams. The non-liquefied ethane plus tail gas stream **125** is combined with the light hydrocarbon stream **111** to form a hydrocarbon gas stream wherein the hydrocarbon gas stream passes into an internal combustion engine **130** to produce power, thus eliminating the negative impact on the environment from flaring the non-liquefied ethane plus tail gas stream and/or reducing the efficiency of the PSA unit and/or requiring a larger unit from recycling it.

In one embodiment of the method of the present invention, the hydrocarbon gas stream resulting from the combination of the non-liquefied ethane plus tail gas stream **125** and the light hydrocarbon stream **111** causes less than 10 percent power output reduction, preferably less than 5 percent power output reduction, most preferably no reduction in power output as compared to the power generated by the light hydrocarbon stream **111** alone.

In one embodiment of the method of the present invention, the heavy hydrocarbon stream **112** has an increased propane, butane, pentane, and/or heavier hydrocarbons (propane plus, C3+) concentration versus that of the natural gas feedstream **101** going into the PSA unit **1** of equal to or greater than 10 mol per cent, more preferably equal to or greater than 20%, most preferably equal to or greater than 30 mol per cent higher C3+ than the natural gas feedstream **101**.

One embodiment of the method of the present invention is for use to incorporate power production to a power grid.

In one embodiment of the method of the present invention, the natural gas feed stream comprises greater than 5 percent C3+ hydrocarbon, preferably greater than 10 percent, more preferably greater than 20 percent C3+ hydrocarbon.

In one embodiment of the method of the present invention, the natural gas feed stream comprises C3 and/or C4 components in an amount greater than individual C5+ contaminants.

In one embodiment of the method of the present invention, the natural gas feed stream has a C3+ hydrocarbon centration of greater than 3 mol%, preferably greater than 8 mol%, more preferably greater than 15 mol%, and more preferably greater than 20 mol%.

One embodiment of the method of the present invention, is for use in an application for flare reduction or flare elimination.

EXAMPLES

A natural gas feedstream having lower heating value (LHV) of 1361 BTU/Sft^3 is used as the feeds for the following examples. A natural gas feedstream having a LHV of 1361 BTU/Sft^3 is too high for efficient power production. In the following examples the natural gas feedstream is separated in a PSA system with 2 alternating adsorption beds, each with a 5 foot diameter, and unless otherwise noted, a height of 15 feet. The PSA operates adsorption at 114.7 psia and regeneration at 4.7 psia. Each of the 3 examples use the same feed gas conditions. Each cycle of the PSA process has an adsorption time of 7.4 mins per bed. Regeneration is assisted by purging with 5.5 lb mol/hr of light hydrocarbon gas for 7.5 minutes per bed. The PSA height is set to achieve a performance of 0.2 mol percent C3 in the light hydrocarbon gas. The heavy hydrocarbon stream enters the liquefaction block which includes compression to 100 psia, cooling to -30°F, and then flashing to 50 psia in a flash tank that allows liquids to drop out. Simulation is performed using Aspen Adsorption with proprietary data obtained for a macroporous polymeric adsorbent available as UCARSORB™ HH Adsorbent from The Dow Chemical Company.

Comparative Example A is a simulation according to the process depicted in **FIG. 2** wherein the non-liquefied ethane plus tail gas stream **122** is flared. Table 1 shows the stream summary of the process for Comparative Example A.

Table 1

	Feed	Light Hydrocarbon	Heavy Hydrocarbon	Liquids	Tail Gas
Mole Flow (lb mol/hr)	109.8	60.9	48.9	19.7	29.2
Temperature (°F)	75	82	60	-30	45
Pressure (psia)	114.7	110.7	16.7	50	50
Component Mole Fraction					
C1	60.0%	88.4%	24.6%	1.4%	40.1%
C2	15.0%	6.6%	25.4%	13.1%	33.8%
C3	15.0%	0.2%	33.5%	50.6%	21.9%
C4	7.0%	0.1%	15.6%	34.9%	2.6%
N2	3.0%	4.7%	0.9%	0.0%	1.5%
Total	100.0%	100.0%	100.0%	100.0%	100.0%
LHV (BTU/Sft^3)	1361	921			

Comparative Example B is a simulation according to the process depicted in **FIG. 2** wherein the non-liquefied ethane plus tail gas stream **122** is recycled back into the PSA unit. In order to maintain the 7.4 minute adsorption time and 0.2% C3 specification for the PSA system, the adsorber height required an increase from 15 to 35 feet of packed adsorbent height. Table 2 shows the stream summary of the process for Comparative Example B.

Table 2

	Feed	Light Hydrocarbon	Heavy Hydrocarbon	Liquids	Liquefaction Recycle
Mole Flow (lb mol/hr)	109.8	76	108.8	19.7	75
Temperature (°F)	75	80	57	-30	45
Pressure (psia)	114.7	109.7	16.7	50	50
Component Mole Fraction					
C1	60.0%	85.6%	23.4%	2.4%	32.8%
C2	15.0%	9.8%	36.1%	26.7%	40.3%
C3	15.0%	0.2%	31.2%	48.2%	23.6%
C4	7.0%	0.1%	8.5%	22.6%	2.2%
N2	3.0%	4.3%	0.8%	0.1%	1.1%
Total	100.0%	100.0%	100.0%	100.0%	100%
LHV (BTU/Sft^3)	1361	947			

Example 1 is a simulation according to the process depicted in **FIG. 3** wherein the non-liquefied ethane plus tail gas stream **125** is combined with the light hydrocarbon stream **111**.

Table 3

	Feed	Light Hydrocarbon	Heavy Hydrocarbon	Liquids	Liquefaction Off Gas	Combined Hydrocarbon
Mole Flow (lb mol/hr)	109.8	60.9	48.9	19.7	29.2	90.1
Temperature (°F)	75	82	60	-30	45	65
Pressure (psia)	114.7	110.7	16.7	50	50	50
Component Mole Fraction						
C1	60.0%	88.4%	24.6%	1.4%	40.2%	72.8%
C2	15.0%	6.6%	25.4%	13.1%	33.8%	15.4%
C3	15.0%	0.2%	33.5%	50.6%	21.9%	7.2%
C4	7.0%	0.1%	15.6%	34.9%	2.6%	0.9%
N2	3.0%	4.7%	0.9%	0.0%	1.5%	3.7%
Total	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%
LHV (BTU/Sft^3)	1361					1112

Power Generation.

Power generation for each of the examples is determined based on the specifications for a Waukesha 16V275GL engine having the following power rating versus gas BTU/Sft^3 shown in Table 4.

Table 4

Gas Feed BTU/Sft^3	% of Standard Rated Load
1026	100
1050	100
1094	98
1419	86

% of Standard Rated Load.

Comparative Example A the Light Hydrocarbons stream feeding a natural gas engine has a LHV of 921 BTU/Sft^3, which allows a Waukesha 16V275GL engine to generate 100% of its rated power. Comparative Example A recovers 69.6% of C3+ from the feedstream as liquids, but 26.6% of the feed gas flowrate exits as liquefaction off gas which would be flared. This system reduces flaring of the feed gas but does not eliminate flaring. The continued presence of flaring poses environmental issues.

For Comparative Example B the Light Hydrocarbons stream feeding a natural gas engine has a LHV of 947 BTU/Sft^3, which allows a Waukesha 16V275GL engine to generate 100% of its rated power. Comparative Example B completely eliminates flaring, however, the increased size of the PSA unit leads to additional equipment and adsorbent costs.

Example 1 requires a packed adsorber height of 15 ft. The combined hydrocarbons stream feeding a natural gas engine has a LHV of 1112 BTU/Sft^3. Interpolation suggests a Waukesha 16V275GL engine would generate 97% of its rated power. The PSA + liquefaction system of the present invention shown for Example 1 completely eliminates flaring of Comparative Example A while incurring a minimal power production penalty. This design does not incur the increased PSA costs of Comparative Example B.

What is claimed is:

1. A method to run a combustion system fueled by a hydrocarbon gas stream wherein the hydrocarbon gas stream is derived from a natural gas feedstream comprising methane and one or more of the natural gas liquids (NGLs): ethane, propane, butane, pentane, or heavier hydrocarbons, wherein some or all of the NGLs are separated from the natural gas feedstream by means of a pressure swing adsorbent (PSA) unit comprising the steps::

(i) providing a natural gas feedstream to the PSA unit comprising an adsorption media,

(ii) separating the natural gas feed stream in the PSA unit into a light hydrocarbon stream and a heavy hydrocarbon stream;

(iii) passing the heavy hydrocarbon stream from the PSA unit to a liquefaction means to produce a liquid hydrocarbons stream and a non-liquefied ethane plus tail gas stream;

(iv) recovering the liquid hydrocarbon stream as a mixture of hydrocarbons and/or further separating it into one or more individual liquid hydrocarbon streams;

(v) combining the light hydrocarbon stream with the non-liquefied ethane plus tail gas stream to form a hydrocarbon gas stream;

and

(vi) providing the hydrocarbon gas stream to power a combustion system.

2. The method of Claim 1 wherein the adsorption media is silica gel, alumina, silica-alumina, a zeolite, activated carbon, a polymer supported silver chloride, a copper-containing resin, a porous cross-linked polymeric adsorbent, a pyrolized macroporous polymer, or mixtures thereof.

3. The method of Claim 1 wherein the adsorption media is a porous cross-linked polymeric adsorbent, a pyrolized macroporous polymer, or mixtures thereof.

4. The method of Claim 1 wherein the combustion system is an internal combustion engine, a furnace, a fired heater, a power plant, or an incinerator and the natural gas feedstream is from an oil well, a gas well, a condensate well, or a natural gas pipeline.

5. The method of Claim 1 wherein the combustion system is an internal combustion engine used to power onsite equipment used for oilfield operations and/or to power

equipment used to maintain and operate natural gas pipelines wherein the source of the natural gas feedstream is from an oil well, a gas well, or a condensate well.

6. The method of Claim 1 wherein the natural gas feed stream comprises greater than 5 percent C3+ hydrocarbon.

7. The method of Claim 1 wherein the natural gas feed stream comprises C3 and/or C4 components in an amount greater than individual C5+ contaminants.

8. The method of Claim 1 wherein the natural gas feed stream has a C3+ hydrocarbon concentration of greater than 3 mol%.

FIG. 1

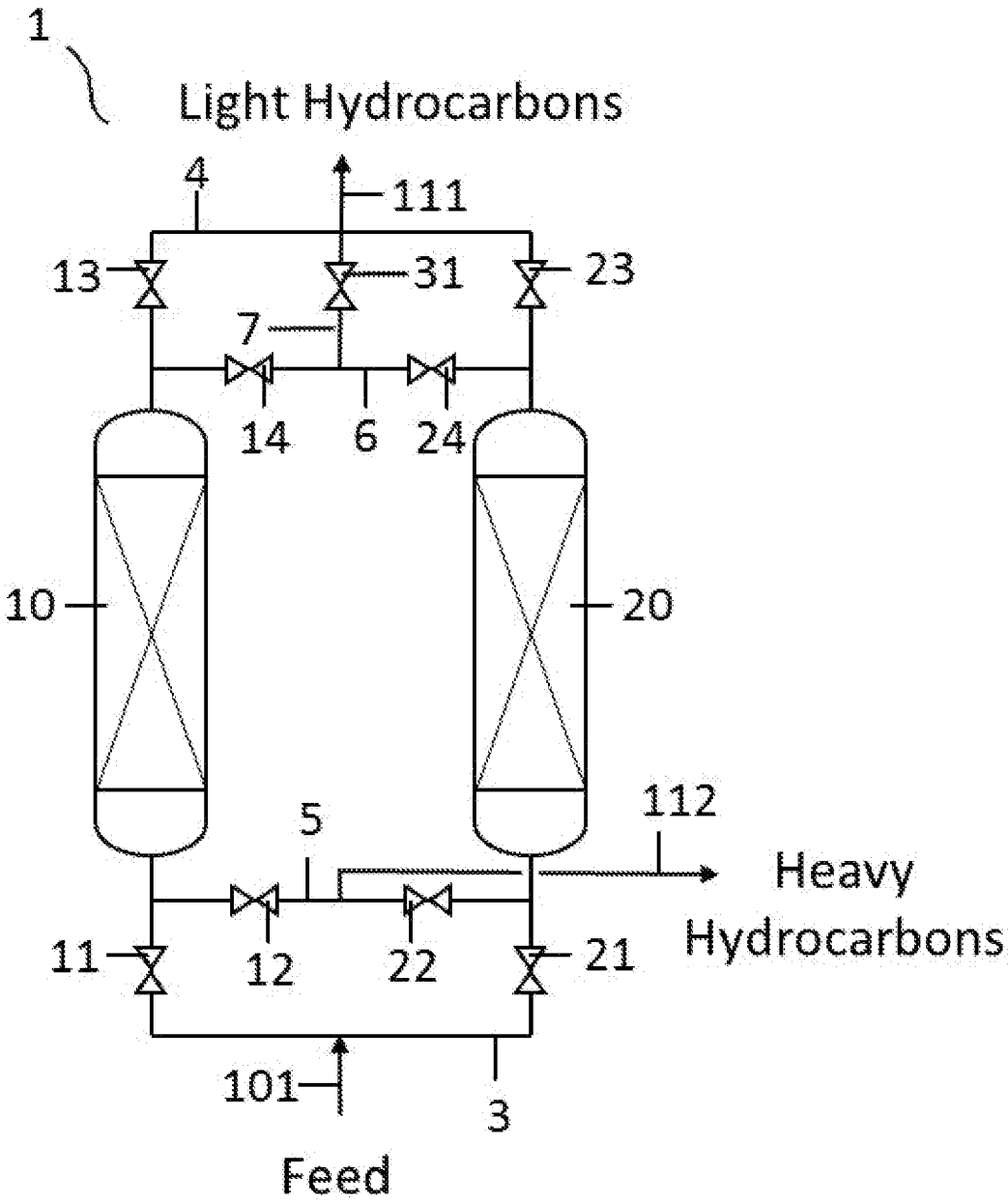

1
Light Hydrocarbons
4
111
13
31
23
7
14
6
24
10
20
112
5
Heavy
Hydrocarbons
11
12
22
21
101
3
Feed

FIG. 2

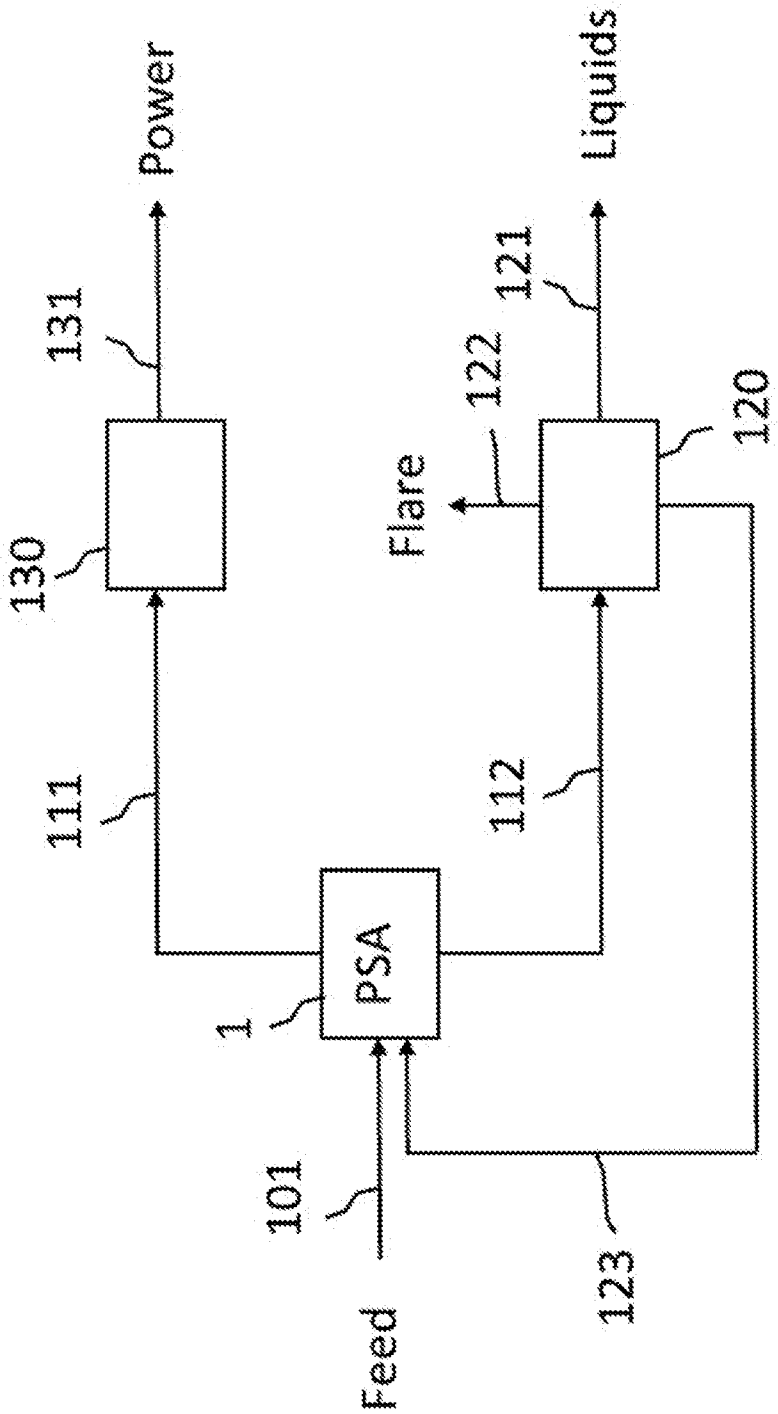
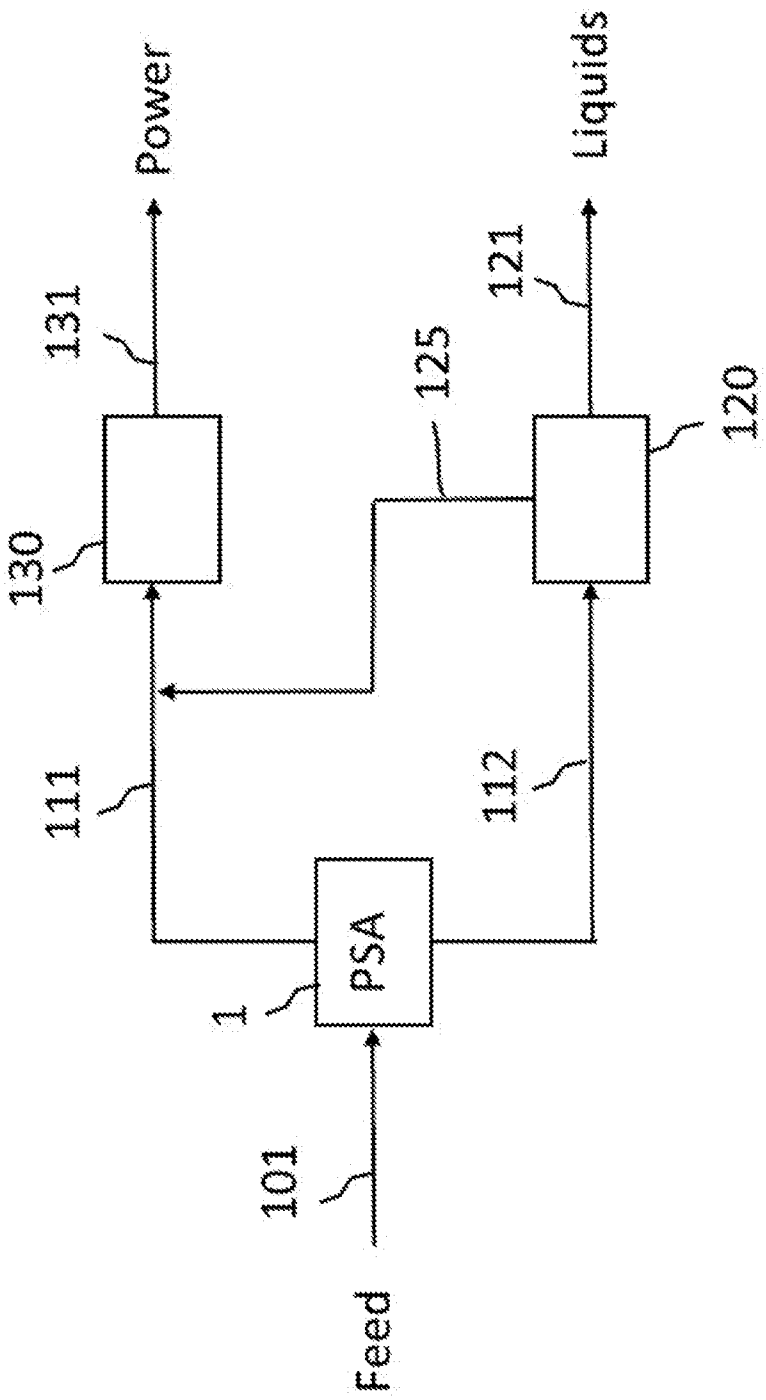

Power
Liquids
131
121
122
Flare
120
130
111
112
PSA
1
101
Feed
123

FIG. 3



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/058003

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/00 B01D53/047 C07C7/13 C10L3/06 C10G5/02
F25J3/06
ADD.
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)
B01D C10L C07C C10G F25J

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)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/222552 A1 (RAVIKOVITCH PETER I [US] ET AL) 6 September 2012 (2012-09-06)	1-8
Y	figure 1 paragraphs [0003], [0040], [0090] - [0092] -----	1-8
Y	DE 10 2008 004077 A1 (MAN DIESEL SE [DE]) 23 July 2009 (2009-07-23) figure 1 claims 1, 5 -----	1-8
Y	US 2016/187057 A1 (MEYER JAMES M [US]) 30 June 2016 (2016-06-30) paragraph [0004] -----	1-8

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 January 2018	23/01/2018

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Pöhlmann, Robert

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2017/058003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2012222552 A1	06-09-2012	AU 2012223552 A1	19-09-2013
		AU 2012223553 A1	19-09-2013
		AU 2012223554 A1	19-09-2013
		AU 2012223558 A1	19-09-2013
		AU 2012223560 A1	11-09-2014
		AU 2012223563 A1	19-09-2013
		AU 2012223564 A1	19-09-2013
		BR 112013020416 A2	18-10-2016
		BR 112013020418 A2	18-10-2016
		BR 112013020763 A2	18-10-2016
		CA 2826900 A1	07-09-2012
		CA 2826907 A1	07-09-2012
		CA 2826908 A1	07-09-2012
		CA 2826928 A1	07-09-2012
		CA 2826987 A1	07-09-2012
		CA 2826989 A1	07-09-2012
		CA 2828457 A1	07-09-2012
		EA 201391188 A1	28-02-2014
		EA 201391189 A1	28-02-2014
		EA 201391190 A1	28-02-2014
		EA 201391191 A1	28-02-2014
		EA 201391192 A1	28-02-2014
		EA 201391193 A1	28-02-2014
		EA 201391194 A1	31-03-2014
		EP 2680940 A2	08-01-2014
		EP 2680941 A1	08-01-2014
		EP 2680943 A1	08-01-2014
		EP 2680944 A1	08-01-2014
		EP 2680945 A1	08-01-2014
		EP 2680951 A1	08-01-2014
		EP 2681705 A2	08-01-2014
		JP 2014508040 A	03-04-2014
		JP 2014509554 A	21-04-2014
		JP 2014509555 A	21-04-2014
		JP 2014509556 A	21-04-2014
		JP 2014509557 A	21-04-2014
		JP 2014512259 A	22-05-2014
		JP 2014514136 A	19-06-2014
		SG 192602 A1	30-09-2013
		SG 192603 A1	30-09-2013
		SG 192604 A1	30-09-2013
		SG 192605 A1	30-09-2013
		SG 192651 A1	30-09-2013
		SG 192653 A1	30-09-2013
		SG 192654 A1	30-09-2013
		US 2012222551 A1	06-09-2012
		US 2012222552 A1	06-09-2012
		US 2012222553 A1	06-09-2012
		US 2012222554 A1	06-09-2012
		US 2012222555 A1	06-09-2012
		US 2012308456 A1	06-12-2012
		US 2012312163 A1	13-12-2012
		WO 2012118736 A2	07-09-2012
		WO 2012118737 A2	07-09-2012
		WO 2012118738 A1	07-09-2012
		WO 2012118742 A1	07-09-2012
		WO 2012118744 A1	07-09-2012
		WO 2012118747 A1	07-09-2012

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2017/058003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		WO 2012118748 A1	07-09-2012
DE 102008004077 A1	23-07-2009	CN 101481635 A	15-07-2009
		DE 102008004077 A1	23-07-2009
		FI 20086234 A	13-07-2009
		JP 5567278 B2	06-08-2014
		JP 2009167411 A	30-07-2009
		KR 20090077874 A	16-07-2009
US 2016187057 A1	30-06-2016	NONE	