Title: IMPROVED CO-CURRENT REGENERATION PROCESS FOR ADSORPTION MEDIA USED FOR RECOVERING CONDENSABLE COMPONENTS FROM A GAS STREAM

Abstract: Disclosed is an improved process for recovering condensable components from a gas stream, in particular, heavier hydrocarbons from a gas stream. The present process uses solid adsorbent media to remove said heavier hydrocarbons wherein the adsorbent media is regenerated in a continuous fashion in a continuous adsorbent media co-current regeneration system using a stripping gas to provide a regenerated adsorbent media and a product gas comprising heavier hydrocarbons from a loaded adsorbent media.
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IMPROVED CO-CURRENT REGENERATION PROCESS FOR ADSORPTION MEDIA
USED FOR RECOVERING CONDENSABLE COMPONENTS FROM A GAS STREAM

FIELD OF THE INVENTION

The present invention relates to an improved process for recovering condensable components such as one or more ethane and heavier hydrocarbons from a gas stream, in particular, for regenerating solid adsorbents used to remove said hydrocarbons. Said process comprises an adsorbent media co-current regeneration system employing a stripping gas.

BACKGROUND OF THE INVENTION

Many various vapor adsorption processes have been developed of the type wherein one or more beds are utilized for adsorbing condensable components from a gas stream while the other beds are being regenerated. In these processes, regeneration of the bed or beds which are saturated with condensable components is accomplished by heating the bed or beds, for example, with a heated regeneration gas stream which causes the condensable components to be desorbed from the bed. The desorbed components are condensed and removed from the regeneration gas stream, and very often are separated into liquid fractions of differing molecular weights. The hot bed which has been regenerated is cooled by contacting it with a cooling gas stream preparatory to again being contacted with the inlet gas stream. The various gas streams are continuously switched or cycled so that the bed or beds which have just contacted the inlet gas stream are contacted with the heated regeneration gas stream, the bed or beds which have just been contacted with the heated regeneration gas stream are contacted with the cooling gas stream, and the bed or beds which have just been contacted with the cooling gas stream are contacted with the inlet gas stream.

Quite often, some of the condensable components adsorbed from a gas stream are difficult to regenerate, i.e., the components are not as readily removed from the adsorbent by contact with a heated regeneration gas stream as are other of the adsorbed condensable components. For example, natural gas usually contains adsorbable hydrocarbon compounds which are relatively easy to regenerate, such as methane, ethane and propane, as well as adsorbable hydrocarbon compounds which are relatively difficult to regenerate, such as butanes and heavier hydrocarbon compounds. In an adsorption process wherein a bed of adsorbent is contacted with a gas stream containing both difficult and easy-to-regenerate adsorbable
components, all of the adsorbable components are adsorbed on the bed to some degree. Generally, the difficult-to-regenerate components are easily adsorbed, and as a result, are adsorbed first followed by the easy-to-regenerate components. Heretofore, such adsorption processes have been designed in a manner allowing for the removal of the difficult-to-regenerate components from the adsorbent even though the primary purpose of the process may be to recover only the easy-to-regenerate components. This has generally been accomplished by contacting the adsorbent with a heated regeneration gas stream at a higher flow rate than would be required to regenerate only the easy-to-regenerate components, or by increasing the cycle time so that the adsorbent is contacted with the regeneration gas stream for a time sufficient to bring about the removal of the difficult-to-regenerate components. An increase in the cycle time of an adsorption process of the type herein described brings about an increase in the quantity of adsorbent material required. Thus, in either case, the equipment required to carry out the process is of a larger overall size and cost as compared to that which would be required to bring about the removal of the easy-to-regenerate components only. As is well understood by those skilled in the art, if difficult-to-regenerate components are not removed from the adsorbent, i.e., if the regeneration gas rate, temperature, or contact time is insufficient to remove all of the adsorbed components, and as a result adsorbed difficult-to-regenerate components remain adsorbed to the adsorbent, the effective life of the adsorbent and the adsorbent's capacity for easy-to-regenerate components decrease rapidly due to the build-up of the difficult-to-regenerate components thereon.

There remains a need for an improved adsorption process for recovering condensable components from a gas stream containing both difficult and easy-to-regenerate condensable components.

SUMMARY OF THE INVENTION

The present invention is an improved adsorption process for recovering condensable components from a gas stream containing both difficult and easy-to-regenerate condensable components wherein the removal of the adsorbed difficult-to-regenerate components from the adsorbent is improved using a stripping gas.

One embodiment of the present invention is an improved process, preferably a continuous process, for separating hydrocarbons from a gas feedstream comprising methane and one or more of ethane, propane, butane, pentane, or heavier hydrocarbons, comprising the steps of: (a) providing one or more adsorbent bed comprising an adsorbent media, such as silica gel, alumina, silica-alumina, zeolites, activated carbon, polymer supported silver chloride, copper-
containing resins, porous cross-linked polymeric adsorbents, pyrolyzed macroporous polymers, or mixtures thereof, wherein said adsorbent media adsorbs one or more ethane, propane, butane, pentane, heavier hydrocarbons, and/or mixtures thereof, (b) passing the gas feedstream through the one or more adsorbent media to provide a methane rich gas stream and a loaded adsorbent media, (c) recovering, transporting, liquefying, or flaring the methane rich gas stream, (d) using co-current regeneration to regenerate the loaded adsorbent media to produce regenerated adsorbent media and a product gas comprising one or more desorbed ethane, propane, butane, pentane, heavier hydrocarbons, and/or mixtures thereof, preferably by using heated gas and/or a radiant heat contact exchanger, more preferably by a using a pressure swing adsorption (PSA) process, a temperature swing adsorption (TSA) process, or a combination thereof, and even more preferably by using a microwave heating system, (e) recovering, transporting, liquefying, re-injecting, excluding, by-passing, or flaring the one or more desorbed ethane, propane, butane, pentane, and/or heavier hydrocarbons individually and/or as mixtures, and (f) reusing the regenerated, preferably the co-current regeneration step of the process of the present invention comprises the use of a stripping gas in the co-current regeneration step, said stripping gas may flow either co-current or counter-current with the loaded adsorbent media being regenerated.

One embodiment of the process of the present invention disclosed herein above the stripping gas comprises a portion of the methane rich gas stream.

In another embodiment of the process of the present invention disclosed herein above the stripping gas comprises a portion of the product gas.

In another embodiment of the present invention, the process described herein above further comprises the steps of (e)(i) passing the product gas through a condenser and optionally a distillation column or knockout to generate two or more product streams comprising at least one product gas vapor stream that comprises generally lighter hydrocarbons and one or more liquid hydrocarbon stream and (e)(ii) using a stripping gas comprising a portion of the product gas vapor stream.

In a preferred embodiment of the process described here in above, the adsorption media is a porous cross-linked polymeric adsorbent, a pyrolyzed macroporous polymer, or mixtures thereof and the regeneration of the loaded adsorbent media is achieved by using a microwave heating system.
BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic of an embodiment of the process for recovering condensable components from a gas stream comprising a co-current regeneration stage according to the invention.

FIG. 2 is a schematic of a second embodiment of a process for recovering condensable components from a gas stream comprising a co-current regeneration stage according to the present invention using a counter-current stripping gas.

FIG. 3 is a schematic of a third embodiment of a process recovering condensable components from a gas stream comprising a co-current regeneration stage according to the present invention using a counter-current stripping gas.

FIG. 4 is a schematic of a fourth embodiment of the process for recovering condensable components from a gas stream comprising a co-current regeneration stage according to the invention using a counter-current stripping gas.

FIG. 5 is a schematic of a fifth embodiment of the process for recovering condensable components from a gas stream comprising a co-current regeneration stage according to the invention using a co-current stripping gas.

FIG. 6 is a schematic of a sixth embodiment of the process for recovering condensable components from a gas stream comprising a co-current regeneration stage according to the invention using a co-current stripping gas.

FIG. 7 is a schematic of a seventh embodiment of the process for recovering condensable components from a gas stream comprising a co-current regeneration stage according to the invention using a co-current stripping gas.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is an improved process to remove condensable components from a gas stream, for example gas streams from a refinery operation, petrochemical operation, or other operations, preferably the gas stream is a natural gas steam. The present process is particularly suitable for gas streams comprising mixtures of two or more of methane, ethane, propane, butane, and/or heavier hydrocarbons. The gas stream may further comprise gasses common to gas streams such as, but not limited to, carbon dioxide (CO$_2$), hydrogen sulfide (H$_2$S), sulfur dioxide (SO$_2$), carbon disulfide (CS$_2$), hydrogen cyanide (HCN), carbonyl sulfide (COS), mercaptans, ethylene, propylene, butenes, and the like.
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 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 (CO₂), hydrogen sulfide (H₂S), sulfur dioxide (SO₂), carbon disulfide (CS₂), 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" (C₂⁺) 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 "methane-rich" refers broadly to any vapor or liquid stream, e.g., after fractionation from which ethane plus amounts have been recovered. Thus, a methane-rich stream has a higher concentration of C₁ than the concentration of C₁ in associated and non-associated natural gas. Preferably, the concentration increase of C₁ is from removal of at least 90 mole percent of the ethane in the natural and removal of at least 95 mole percent of the propane plus.

Suitable adsorbents for use in the process of the present invention are solids having a microscopic structure. The internal surface of such adsorbents is preferably between 100 to 2000 m²/g, more preferably between 500 to 1500 m²/g, and even more preferably 1000 to 1300 m²/g. The nature of the internal surface of the adsorbent in the adsorbent bed is such that light hydrocarbons (C₂ and C₃) and heavier hydrocarbons (C₄⁺) 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 pyrolyzed macroporous polymer. Preferably, the internal surface of the adsorbent is non-polar.
In one embodiment, the process of the present invention uses an adsorbent media to extract NGLs from a natural gas stream. The mechanism by which the macroporous polymeric adsorbent extracts 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 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 "macoreticular" 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 process 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, vinlyltoluene, 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, and 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 m²/g, and preferably from about 400 to about 1400 m²/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 ambient temperature and 10°C to 15°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 300 psig (2170 kPa). The residence time of the natural gas stream in the adsorbent bed will most often range from 0.02 second to 5 seconds, and preferably from 0.3 second to 3.0 seconds. The space velocity of the natural gas stream through the bed will most often fall within the range of 0.1 foot per second to 5 feet per second, with a range of 0.3 foot per second to 3 feet per second preferred. Finally, the relative humidity can have any value up to 100%, although for convenience, the preferred range of relative humidity is about 25% to about 98%.

The macroporous polymeric adsorbents of the present invention described herein above can be used to separate ethane, propane, butane, pentane, and heavier hydrocarbons from mixed gases containing methane. Preferably, the macroporous polymeric adsorbents of the present invention adsorb equal to or greater than 60 cm³ 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 cm³ 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 cm³ STP of propane per gram of sorbent at 35°C and 500 mmHg of propane or readsorb greater than 60 cm³ 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 cm³ 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 cm³ STP of pentane per gram of sorbent at 35°C and 50 mmHg of pentane.

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

Pyrolyzed 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 macroporous 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 contains 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 useful in the process of the present 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 m²/gram. Of this, the macropores will normally contribute 6 to 700 m²/gram, preferably 6 to 200 m²/gram, 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 C0₂, N₂, O₂, H₂O 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, ethoxycyclohexyl, hydroxyethyl, hydroxypropyl, ethylene, propylene, isobutyene, diisobutylenec, 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, divinylsulfide, 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 tricarboxylate, triallyl aconitate, triallyl citrate, triallyl phosphate, \( N,N' \)-methylenediacrylamide, \( N,N' \)-methylenehexamethacrylamide, \( N,N' \)-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 xylene, and ethylvinylbenzene.

Examples of preferred polyethylenically unsaturated compounds include divinyl pyr dine, divinyl naphthalene, divinylbenzene, trivinylbenzene, alkyldivinylbenzenes having from 1 to 4 alkyl groups of 1 to 2 carbon atoms substituted in the benzene nucleus, and alkyltrivinylbenzene 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-hydroxybenzoic 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’-methyleneedianilne, 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.; (l) 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/hour to 600 bedvolume/min. preferably 10 to 200 bedvolume/minute.

The partially pyrolyzed macroporous polymer adsorbent useful in process of the present invention disclosed herein above are able to adsorb greater than 25 cm³ STP of ethane per gram of sorbent at 35°C and 200 mmHg of ethane and greater than 30 cm³ 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 readsoorb greater than 25 cm³ STP of ethane per gram of sorbent at 35°C and 200 mmHg of ethane, or readsoorb greater than 30 cm³ STP of propane per gram of sorbent at 35°C and 100 mmHg of propane or more times.

In the process of the present invention, the adsorption of hydrocarbons by the adsorbing media is a reversible process. The practice of removing volatiles from a loaded adsorption media can be accomplished by any suitable means, typically by reducing the pressure over the media, heating, or the combination of reduced pressure and heating. In either case the desired outcome is to re-volatilize the trapped vapors, and subsequently remove them from the adsorbent media so that it can be reused to capture additional volatiles. Preferably, the adsorption media of the present invention when regenerated, desorbs adsorbed gases in an amount equal to or greater than 75 percent of the amount adsorbed, more preferably equal to or greater than 85 percent, more preferably equal to or greater than 90 percent, more preferably equal to or greater than 95 percent, more preferably equal to or greater than 99 percent and most preferably virtually all the NGLs adsorbed.

Traditional means of heating adsorbent media for the purpose of removing adsorbed
volatiles that utilize conventional heating systems such as heated gas (air or inert gas), or radiant heat contact exchangers are suitable for use in the present NGL separation process as part of the adsorbent media regeneration step, for example, by a pressure swing adsorption (PSA) process, a temperature swing adsorption (TSA) process, or a combination thereof. Preferably, the NGL separation process of the present invention employs a microwave heating system as part of the adsorbent media regeneration step. Such a microwave heating system provides a heating system and method for removing volatiles from adsorbent media with higher thermal efficiency at a reduced cost.

The process of the present invention may be operated where the absorbent is stationary and different gases are fed to the column, or in a moving bed process, where the absorbent is cycled through different adsorption and desorption units.

Now referring to the diagrams, the process of the present invention comprises co-current regeneration of loaded adsorbent (FIG. 1). The process of the present invention may further comprise the use of a stripping gas. The stripping gas may flow counter-current (FIGS. 2 to 4) or flow co-current with the regeneration of the loaded adsorbent (FIGS. 5 to 7) to the regeneration of the loaded adsorbent.

A first embodiment of the separation process of the present invention for removing hydrocarbons (e.g., natural gas liquids) from a gas feedstream is shown in FIG. 1. In the separation process a gas feedstream is passed 3 into an adsorption unit 10 comprising an adsorbent bed 2 comprising an adsorbent media which adsorbs one or more of ethane and heavier hydrocarbons (C₂, C₃, C₄, C₅, etc.) to obtain a methane rich gas product 4 which is discharged 5 (recovered, transported through pipeline or other means, liquefied, flared or the like). The adsorbent loaded with one or more of ethane and heavier hydrocarbons is transporting 11 from the adsorption unit 10 to a co-current regeneration unit 20.

The co-current regeneration unit comprises a means 32 to regenerate the loaded adsorbent media and produce regenerated product gas 33 comprising the desorbed one or more of ethane and heavier hydrocarbons. Said co-current regeneration unit comprising an optional heating means 30 whereby causing the release of one or more of ethane and heavier hydrocarbons from the loaded adsorbing media and forming regenerated adsorbent media 23. Both the regenerated adsorption media 23 and the regenerated product gas 33 exits the bottom of the co-current regeneration unit 21. The regenerated adsorbent media 23 is transported through line 8 back to the adsorption unit 10 for reuse. The released product gas 33 comprising one or more ethane and heavier hydrocarbons is discharged through line 29, (e.g., recovered, re-injected, excluded, by-passed, or flared) as either as a mixture or individually as gas (e.g., as C₂, C₃, C₄, etc.).
C3, C4, C5, etc.), passed through a compressor 50, into a condenser (or knockout) 60 where the one or more of ethane and heavier hydrocarbons are liquefied and recovered either as a mixture or individually as separate liquids and any uncondensed gas (such as C1 and/or C2) is discharged (recovered, flared, or the like) 61.

To provide continuous operation, there is a valve 12 in line 11 between the adsorber tank 1 and the regeneration tank 21 and a valve 27 in the line 26 between the regeneration tank 21 and collection tank 17. Valves 12 and 27 are synchronized to allow for holding loaded adsorption media from the adsorption tank 1 while adsorption media is being regenerated in the regenerator unit 20. When the adsorption media is regenerated in the regenerator tank 21, valve 27 allows the regenerated adsorption media 23 to pass from the bottom of the regeneration tank 21 through line 26 into the holding tank 17 and then to be transported back to the adsorption tank 1 through line 8. A portion of the methane rich gas from the top of the adsorber tank 1 is circulated via line 6 through blower 7 to transport the regenerated adsorption media 23 through line 8 to once again adsorb NGLs from a gas feedstream 3. Valve 12 is synchronized with valve 27 to allow loaded adsorption media to enter the regenerator tank 21 to be regenerated. This process is repeated and allows for a continuous regeneration of the adsorption media. In such a conventional co-current regeneration process no stripping gas 25 is utilized.

Now referring to FIG. 2, a second embodiment of the separation process of the present invention for removing hydrocarbons (e.g., natural gas liquids) from a gas feedstream is shown which uses a stripping gas that flows counter-current to the regeneration of the loaded adsorbent media. In the separation process a gas feedstream 3 is passed into an adsorption unit 10 comprising an adsorbent bed 2 comprising an adsorbent media which adsorbs one or more of ethane and heavier hydrocarbons (C2, C3, C4, C5, etc.) to obtain a methane rich gas product 4 which is discharged 5 (recovered, transported through pipeline or other means, liquefied, flared or the like). The adsorbent loaded with one or more of ethane and heavier hydrocarbons is transported 11 from the adsorption unit 10 to a co-current regeneration unit 20 utilizing a counter-current stripping gas 25 to produce regenerated product gas 33 comprising the desorbed one or more of ethane and heavier hydrocarbons and regenerated adsorption media 23. The regenerated adsorbent media 23 and regenerated product gas 33 exits the bottom of the co-current regeneration unit 21. The regenerated adsorbent media 23 is transported through line 8 back to the adsorption unit 10 for reuse.

The co-current regeneration unit 20 comprises a microwave heating system 32 with a microwave power source 30. The source of the stripping gas 25 is a portion of the methane rich gas 4 from the top of the adsorber tank 1 circulated via line 6 through blower 7, valve 18, line
19, line 26, and into the bottom of the regeneration tank 21 to facilitate stripping adsorbed hydrocarbons from the loaded adsorbent media.

The product gas 33 passes through line 29 through a gas compression system 50 and into an optional condenser (knockout) 60 which generates two or more product streams comprising at least one product gas vapor stream 61 that comprises generally lighter hydrocarbons (e.g., one or more of methane and/or lighter hydrocarbons (e.g., C₂ and C₃)) and/or other gases and one or more liquid hydrocarbon stream whose composition is dictated by the well known influence of pressure, temperature and composition of 29 (e.g., one or more of C₄+). The one or more liquid stream are discharged either as a mixture of hydrocarbons or optionally separated into individual fractions of one or more of ethane, propane, butane, pentane, and/or other heavier hydrocarbons. The discharged liquid hydrocarbons may be recovered, transported, re-injected, excluded, by-passed, or flared. The product gas vapor stream comprising one or more of methane and/or lighter hydrocarbons (e.g., C₂ and C₃) and/or other gases s may be vented, collected, or recycled back to the adsorption tank 1 through line 61.

In one embodiment of the present invention, the hydrocarbon separation process is a continuous process with continuous adsorbent media regeneration. In FIG. 2 there is a valve 12 in line 11 between the adsorber tank 1 and the regeneration tank 21 and a valve 27 in the line 26 between the regeneration tank 21 and collection tank 17. Valves 12 and 27 are synchronized to allow for holding loaded adsorption media from the adsorption tank 1 while adsorption media is being regenerated in the regenerator unit 20. When the adsorption media is regenerated in the regenerator tank 21, valve 27 allows the regenerated adsorption media 23 to leave the regenerator tank 21 and be transported back to the adsorption tank 1. Then valve 12 allows loaded adsorption media to enter the regenerator tank 21 to be regenerated. This process is repeated and allows for a continuous regeneration of the adsorption media.

Now referring to FIG. 3, a third embodiment of the separation process of the present invention for removing hydrocarbons (e.g., natural gas liquids) from a gas feedstream is shown which uses a stripping gas that flows counter-current to the regeneration of the loaded adsorbent media. In the separation process a gas feedstream 3 is passed through an adsorption unit 10 comprising an adsorbent bed 2 comprising an adsorbent media which adsorbs one or more of ethane and heavier hydrocarbons (C₂, C₃, C₄, C₅, etc.) to obtain a methane rich gas product 4 which is discharged 5 (recovered, transported through pipeline or other means, liquefied, flared or the like). The adsorbent loaded with one or more of ethane and heavier hydrocarbons is transported 11 from the adsorption unit 10 to a co-current regeneration unit 20 utilizing a
counter-current stripping gas 25 to produce regenerated product gas 33 comprising the desorbed one or more of ethane and heavier hydrocarbons and regenerated adsorption media 23. The regenerated adsorbent media 23 and regenerated product gas 33 exits the bottom of the co-current regeneration unit 21. The regenerated adsorbent media 23 is transported through line 8 back to the adsorption unit 10 for reuse.

The co-current regeneration unit 20 comprises a microwave heating system 32 with a microwave power source 30. The source of the stripping gas 25 is a portion of the regenerated product gas 33 that is diverted after leaving the bottom of the regeneration unit 21 before being subjected to any other process steps (e.g., condensed, distilled, and the like) 35. The portion of the regenerated product gas 33 which becomes the stripping gas 25 is circulated through line 36, blower 37, line 19, line 26, and into the bottom of the regeneration tank 21.

The portion of the product gas 33 not used as stripping gas 25 passes through line 29 through a gas compression system 50 and into an optional condenser (knockout) 60 which generates two or more product streams comprising at least one product gas vapor stream 61 that comprises generally lighter hydrocarbons (e.g., one or more of methane and/or lighter hydrocarbons (e.g., C₂ and C₃)) and/or other gases and one or more liquid hydrocarbon stream whose composition is dictated by the well known influence of pressure, temperature and composition of 29 (e.g., one or more of C₄⁺). The one or more liquid stream are discharged either as a mixture of hydrocarbons or optionally separated into individual fractions of one or more of ethane, propane, butane, pentane, and/or other heavier hydrocarbons. The discharged liquid hydrocarbons may be recovered, transported, re-injected, excluded, by-passed, or flared. The product gas vapor stream comprising one or more of methane and/or lighter hydrocarbons (e.g., C₂ and C₃) and/or other gases s may be vented, collected, or recycled back to the adsorption tank 1 through line 61.

In one embodiment of the present invention, the hydrocarbon separation process is a continuous process with continuous adsorbent media regeneration. In FIG. 3 there is a valve 12 in line 11 between the adsorber 1 and the regeneration tank 21 and a valve 27 in the line 26 between the regeneration tank 21 and collection tank 17. Valves 12 and 27 are synchronized to allow for holding loaded adsorption media from the adsorption tank 1 while adsorption media is being regenerated in the regenerator unit 20. When the adsorption media is regenerated in the regenerator tank 21, valve 27 allows the regenerated adsorption media 23 to leave the regenerator tank 21 and be transported back to the adsorption tank 1. Then valve 12 allows loaded adsorption media to enter the regenerator tank 21 to be regenerated. This process is repeated and allows for a continuous regeneration of the adsorption media.
Now referring to FIG. 4, a fourth embodiment of the separation process of the present invention for removing hydrocarbons (e.g., natural gas liquids) from a gas feedstream is shown which uses a stripping gas that flows counter-current to the regeneration of the loaded adsorbent media. In the separation process a gas feedstream 3 is passed through an adsorption unit 10 comprising an adsorbent bed 2 comprising an adsorbent media which adsors one or more of ethane and heavier hydrocarbons (C₂, C₃, C₄, etc.) to obtain a methane rich gas product 4 which is discharged 5 (recovered, transported through pipeline or other means, liquefied, flared or the like). The adsorbent loaded with one or more of ethane and heavier hydrocarbons is transported 11 from the adsorption unit 10 to a co-current regeneration unit 20 utilizing a counter-current stripping gas 25 to produce regenerated product gas 33 comprising the desorbed one or more of ethane and heavier hydrocarbons and regenerated adsorption media 23. The regenerated adsorbent media 23 and regenerated product gas 33 exits the bottom of the co-current regeneration unit 21. The regenerated adsorbent media 23 is transported through line 8 back to the adsorption unit 10 for reuse.

The co-current regeneration unit 20 comprises a microwave heating system 32 with a microwave power source 30. The product gas 33 passes through line 29 through a gas compression system 50 and into an optional condenser (knockout) 60 which generates two or more product streams comprising at least one product gas vapor stream 61 that comprises generally lighter hydrocarbons (e.g., one or more of methane and/or lighter hydrocarbons (e.g., C₂ and C₃)) and/or other gases and one or more liquid hydrocarbon stream whose composition is dictated by the well known influence of pressure, temperature and composition of 29 (e.g., one or more of C₄+). The one or more liquid stream are discharged either as a mixture of hydrocarbons or optionally separated into individual fractions of one or more of ethane, propane, butane, pentane, and/or other heavier hydrocarbons. The discharged liquid hydrocarbons may be recovered, transported, re-injected, excluded, by-passed, or flared.

A portion of the product gas vapor stream may be vented, collected, or recycled back to the adsorption tank 1 through line 61. Another portion of the product gas vapor stream is the source of the stripping gas 25. The portion of product gas vapor stream used as stripping gas 25 is diverted 65 back to the co-current regeneration unit 20 through line 66, blower 37, line 19, line 26, and into the bottom of the regeneration tank 21. With lower concentrations of heavier hydrocarbons, the stripping gas 25 of this embodiment of the present process will be more efficient at diluting the concentration of heavier hydrocarbons at the bottom of the regenerator tank 21 making them easier to separate from the adsorbent material.
In one embodiment of the present invention, the hydrocarbon separation process is a continuous process with continuous adsorbent media regeneration. In FIG. 3 there is a valve 12 in line 11 between the adsorber tank 1 and the regeneration tank 21 and a valve 27 in the line 26 between the regeneration tank 21 and collection tank 17. Valves 12 and 27 are synchronized to allow for holding loaded adsorption media from the adsorption tank 1 while adsorption media is being regenerated in the regenerator unit 20. When the adsorption media is regenerated in the regenerator tank 21, valve 27 allows the regenerated adsorption media 23 to leave the regenerator tank 21 and be transported back to the adsorption tank 1. Then valve 12 allows loaded adsorption media to enter the regenerator tank 21 to be regenerated. This process is repeated and allows for a continuous regeneration of the adsorption media.

Now referring to FIG. 5, a fifth embodiment of the separation process of the present invention for removing hydrocarbons (e.g., natural gas liquids) from a gas feedstream is shown which uses a portion of the methane rich gas 4 as the stripping gas 25. The process is the same as the process described in FIG. 2, except the stripping gas 25 is fed into the top (instead of the bottom) of the regeneration tank 21 and flows co-current with the regeneration of the loaded adsorbent media.

Now referring to FIG. 6, a sixth embodiment of the separation process of the present invention for removing hydrocarbons (e.g., natural gas liquids) from a gas feedstream is shown which uses a portion of the product gas 33 as the stripping gas 25. The process is the same as the process described in FIG. 3, except the stripping gas 25 is fed into the top (instead of the bottom) of the regeneration tank 21 and flows co-current with the regeneration of the loaded adsorbent media.

Now referring to FIG. 7, a seventh embodiment of the separation process of the present invention for removing hydrocarbons (e.g., natural gas liquids) from a gas feedstream is shown which uses a portion of the product gas vapor stream 61 as the stripping gas 25. The process is the same as the process described in FIG. 4, except the stripping gas 25 is fed into the top (instead of the bottom) of the regeneration tank 21 and flows co-current with the regeneration of the loaded adsorbent media.

While only a few preferred embodiments of the process of the present invention are described in the diagrams, it should now be apparent to those skilled in the art, how alternative embodiments may implement the purposes of the present invention. For example, the stripping gas can comprise any suitable gas (a) other than the methane rich gas stream, product gas, or product gas vapor stream, for example nitrogen, a source of hydrocarbon gas other than the process of the present invention, etc., and/or (b) in addition to the methane rich gas stream,
product gas, or product gas vapor stream of the present invention, e.g., a portion of the methane rich gas stream with one or more other gasses, or a portion of the product gas with one or more other gasses, or the a portion of the product gas vapor stream with one or more other gasses. As such, the invention can only be construed and limited in its breadth by the scope of the claims that follow.
What is claimed is:

1. A process for separating hydrocarbons from a gas feedstream comprising methane and one or more of ethane, propane, butane, pentane, or heavier hydrocarbons, comprising the steps of:

   (a) providing one or more adsorbent bed comprising an adsorbent media, wherein said adsorbent media adsorbs one or more of ethane, propane, butane, pentane, heavier hydrocarbons, and/or mixtures thereof,

   (b) passing the gas feedstream through the one or more adsorbent bed to provide a methane rich gas stream and a loaded adsorbent media,

   (c) recovering, transporting, liquefying, or flaring the methane rich gas stream,

   (d) using co-current regeneration to regenerate the loaded adsorbent media to produce regenerated adsorbent media and a product gas comprising one or more desorbed ethane, propane, butane, pentane, heavier hydrocarbons, and/or mixtures thereof,

   (e) recovering, transporting, liquefying, re-injecting, excluding, by-passing, or flaring the one or more desorbed ethane, propane, butane, pentane, and/or heavier hydrocarbons individually and/or as mixtures, and

   (f) reusing the regenerated adsorbent media.

2. The process of Claim 1 wherein the co-current regeneration step further comprises the use of a stripping gas wherein the flow of the stripping gas may be co-current or counter-current to the regeneration of the loaded adsorbent media.

3. The process of Claim 2 wherein the stripping gas comprises a portion of the methane rich gas stream.

4. The process of Claim 2 wherein the stripping gas comprises a portion of the product gas.

5. The process of Claim 2 further comprising the steps

   (e)(i) passing the product gas through a condenser and optionally a distillation column or knockout to generate two or more product streams comprising at least one product gas vapor stream that comprises generally lighter hydrocarbons and one or more liquid hydrocarbon stream

   and

   (e)(ii) using a stripping gas comprising a portion of the product gas vapor stream.
6. The process of Claim 1 wherein the adsorption media is silica gel, alumina, silica-
alumina, zeolites, activated carbon, polymer supported silver chloride, copper-containing resins, porous cross-linked polymeric adsorbents, pyrolized macroporous polymers, or mixtures thereof.

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

8. The process of Claim 1 wherein the regeneration of the loaded adsorbent is achieved by using heated gas and/or a radiant heat contact exchanger.

9. The process of Claim 1 wherein the regeneration of the loaded adsorbent media is achieved by using a pressure swing adsorption (PSA) process, a temperature swing adsorption (TSA) process, or a combination thereof.

10. The process of Claim 1 wherein the regeneration of the loaded adsorbent media is achieved by using a microwave heating system.

11. The process of Claim 1 wherein the process is continuous.

12. The process of Claim 1 wherein the adsorption media is a porous cross-linked polymeric adsorbent, a pyrolized macroporous polymer, or mixtures thereof and the regeneration of the loaded adsorbent media is achieved by using a microwave heating system.
A. CLASSIFICATION OF SUBJECT MATTER

INV. B01D53/04 C10L3/10 C10G5/02 B01D53/08
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols):
B01D CIOL CIOG

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**

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<th>Category</th>
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<td>US 2011/315012 AI (KUZNICKI STEVEN MITCHELL [CA] ET AL) 29 December 2011 (2011-12-29) paragraphs [0020], [0021], [0027] - [0035], [0111] - [0119] figure 6 example 4</td>
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[X] Further documents are listed in the continuation of Box C.  

"*" Special categories of cited documents:
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"A" document member of the same patent family

Date of the actual completion of the international search: 12 January 2015

Date of mailing of the international search report: 23/01/2015

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

Authorized officer: Hackenberg, Stefan
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