

IMPROVED HYDROGEN MANAGEMENT FOR HYDROPROCESSING UNITS

FIELD OF THE INVENTION

[0001] This invention relates to improved hydroprocessing processes for upgrading refinery streams via the use of rapid cycle pressure swing adsorption having a cycle time of less than one minute for increasing the concentration of hydrogen for use in hydroprocessing units.

BACKGROUND OF THE INVENTION

[0002] Hydroprocessing processes are used by petroleum refiners to improve the properties and hence value of many refinery streams. Such hydroprocessing units include hydrotreating, hydrocracking, hydroisomerization and hydrogenation process units. Hydroprocessing is generally accomplished by contacting a hydrocarbon feedstock in a hydroprocessing reaction vessel, or zone, with a suitable hydroprocessing catalyst under hydroprocessing conditions of elevated temperature and pressure in the presence of a hydrogen-containing treat gas to yield an upgraded product having the desired product properties, such as sulfur and nitrogen levels, boiling point, aromatic concentration, pour point and viscosity index. The operating conditions and the hydroprocessing catalysts used will influence the quality of the resulting hydroprocessing products.

[0003] Several types of hydroprocessing operations are practiced commercially in refining operations. For example, hydrotreating is typically used to remove heteroatoms, such as sulfur and nitrogen, from hydrocarbon feedstreams such as naphtha, kerosene, diesel, gas oil, vacuum gas oil (VGO), and residua, by

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contacting the feedstream with hydrogen and a suitable hydrotreating catalyst, at hydrotreating conditions of temperature, pressure and flow rates to result in the heteroatoms being converted to hydrogen sulfide. Hydrotreaters are also employed to improve other properties of hydrocarbon streams in the refinery. Hydrocracking is typically used to remove sulfur and nitrogen, and to reduce the boiling point of heavier molecules by converting them into lighter molecules, by contacting the feedstream with hydrogen and a suitable hydrocracking catalyst, at hydrocracking process conditions. Hydrodewaxing and hydroisomerization of distillate and lubricating oils modifies the molecular structure and hence the pour point of these molecules, by contacting the feedstream with hydrogen over a suitable catalyst, at hydrodewaxing and hydroisomerization process conditions. Hydroprocessing for olefin and aromatic saturation reduces the concentration of aromatics and olefins by contacting the feedstream with hydrogen over a suitable catalyst at aromatic/olefin saturation conditions.

[0004] All of these hydroprocessing operations require the use of hydrogen, and the amount of hydrogen required to operate these hydroprocessing units has greatly increased for several reasons. Regulatory pressure in the United States, Europe, Asia, and elsewhere has resulted in a trend to increasingly severe and/or selective hydroprocessing processes to form hydrocarbon products having very low levels of sulfur and other tailored properties, such as reduced aromatics levels, and improved pour point and viscosity index. The move to process heavier crude oils and the reduced market for fuel oil is increasing the need for hydrocracking, again leading to a higher hydrogen demand. As the qualities of lubricating oils improve, the need to remove even more sulfur, reduce aromatics levels, and improve pour point and viscosity index have increased the need for hydroprocessing. Further, many refineries receive large amounts of hydrogen as a by-product of catalytic reforming on their site. However, current trends to reduce aromatics in gasoline are

constraining the use of catalytic reforming and thus removing a source of hydrogen. Thus, there is an ever growing need for improved hydrogen management associated with the various process units.

[0005] Hydroprocessing units use relatively large quantities of hydrogen that are often obtained from process units that generate hydrogen, either as a main product stream or as a side product stream. The vapor phase product stream from hydroprocessing units typically contains unreacted hydrogen that is recycled to the hydroprocessing reaction zone. Since hydrogen is an important reactant in hydroprocessing, economic means to purify hydrogen in hydrogen-containing streams used as feed streams and/or as recycle streams is desirable. A greater concentration of hydrogen in either of these two types of hydrogen-containing streams allows for a more efficient process with higher feed throughput.

[0006] The type of feed to be processed, product quality requirements, yield, and the amount of conversion for a specific catalyst cycle life determines the hydrogen partial pressure required for the operation of a hydroprocessing unit. The unit's operating pressure and the recycle gas purity determine the hydrogen partial pressure of the hydroprocessing unit. Since there is limited control over the composition of the flashed gas from the downstream hydroprocessor separator or flash drum, the hydrogen composition of the recycle flash gas limits the hydrogen partial pressure ultimately delivered to the hydroprocessor reactor. A relatively lower hydrogen partial pressure in the recycle gas stream effectively lowers the partial pressure of the hydrogen gas input component to the reactor and thereby adversely affects the operating performance with respect to product quantity and quality, catalyst cycle life, etc. To offset this lower performance, the operating pressure of the hydroprocessor reactor has to be increased, which can be undesirable from an operational point of view. Conversely, by increasing the

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efficiency of hydrogen gas recovery and hydrogen concentration, the hydrogen partial pressure of the recycle gas stream is improved. This results in an overall improved performance of the hydroprocessing process unit as measured by these parameters.

[0007] Some conventional methods have been proposed that attempt to improve the hydrogen utilization efficiency of the hydroprocessing unit by increasing the concentration of the hydrogen in the recycle gas stream. Such processes typically result in significant additional equipment costs and/or require significant changes in operating conditions, such as temperature and pressure, which typically results in increased capital and operating costs.

[0008] One process that has been adopted to improve the hydrogen purity of the recycle stream in a hydroprocessing unit is conventional pressure swing adsorption (CPSA). See, for example, U.S. Pat. No. 4,457,384 issued Jul. 3, 1984 to Lummus Crest, Inc. However, in order to incorporate the PSA unit, the pressure of the reactor effluent gas stream must be reduced from about 2,500 psig (175.8 kg/cm²) to about 350 psig (24.6 kg/cm²). Although the purity of the recycle hydrogen stream can be increased to about 99 mol %, the recycled gaseous stream must be subjected to compression to return it to 2,500 psig (175.8 kg/cm²) before introduction into the hydroprocessing feed stream. The net result is that the capital, operating and maintenance costs are substantially increased by the addition of a large compressor that is required when using a conventional PSA unit.

[0009] Another method is described in U.S. Pat. No. 4,362,613 to MacLean which is incorporated herein by reference. MacLean uses membranes with pressure drops up to 150 atmospheres and which also incurs substantial capital investment and operating costs.

[0010] There is therefore a need for an improved process for enhancing the efficiency of hydrogen utilization by means that are compatible with existing hydroprocessing units. It is desired that such a process would not adversely affect the hydroprocessor throughput or the overall economies of the system, including capital expenditures and operating expenditures, the latter including maintenance and energy consumption.

[0011] In other words, although various hydroprocessing processes are practiced commercially, there is still a need in the art for improved hydroprocessing processes that can be practiced more efficiently and with higher reactor throughput by combining improvements to hydrogen recovery and purification with hydroprocessing units.

SUMMARY OF THE INVENTION

[0012] In a preferred embodiment, there is provided a process for upgrading a hydrocarbon feed in a hydroprocessing process unit, comprising:

- a) contacting said hydrocarbon feed in a hydroprocessing zone with hydrogen, a portion of which is obtained from a hydrogen-containing make-up gas, and a catalytically effective amount of a hydroprocessing catalyst at hydroprocessing conditions thereby resulting in a liquid phase and a vapor phase product;
- b) separating said liquid phase and said vapor phase, which vapor phase contains hydrogen and light hydrocarbons;
- c) removing at least a portion of the light hydrocarbons from the hydrogen-containing make-up treat gas, the vapor phase product, or both, in a rapid cycle pressure swing adsorption unit containing a plurality of adsorbent beds and

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having a total cycle time of less than about 30 seconds and a pressure drop within each adsorbent bed of greater than about 5 inches of water per foot of bed length;

d) recycling at least a portion of the vapor phase of step c) above having a higher concentration of hydrogen to the hydroprocessing zone.

[0013] In another preferred embodiment, the hydrocarbon feed is selected from the group consisting of naphtha boiling range feeds, kerosene and jet fuel boiling range feeds, distillate boiling range feeds, residues and crudes.

[0014] In yet another preferred embodiment, the total cycle time or the rapid cycle pressure swing adsorption step is less than about 15 seconds.

[0015] In still another preferred embodiment the total cycle time is less than about 10 seconds and the pressure drop is greater than about 10 inches of water per foot of bed length for the rapid cycle pressure swing adsorption step.

DETAILED DESCRIPTION OF THE INVENTION

[0016] It has been recognized that by increasing the efficient use of hydrogen, existing equipment could be employed to increase the throughput of the feedstock resulting in higher product yields. A further advantage to the more efficient utilization of hydrogen is the reduction in the amount of make-up hydrogen that must be provided by, for example, a hydrogen plant, cryo-unit or reformer.

[0017] The instant invention is applicable to any unit in a petroleum refinery that uses hydrogen as a treat-gas stream, or as a recycle stream, or produces hydrogen as a primary product or as a side product stream. It is particularly applicable to those process units that use hydrogen as a reactant to upgrade or to

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convert a hydrocarbon stream to lower boiling products. Such process units are typically referred to as hydroprocessing units. The art has long recognized the importance of improving the purity (concentration) of hydrogen in the recycle stream of hydroprocessing units. Non-limiting types of hydroprocessing that are included herein are: hydrotreating wherein light hydrocarbon, naphtha, diesel, distillate, atmospheric and vacuum gas oils, kerosene, jet, cycle oils, lubestock and waxes, atmospheric and vacuum residua, pyrolysis gasoline, and crude streams are upgraded by the removal of heteroatoms, hydrogenation wherein double bonds are converted to olefins and paraffins and aromatics are saturated to naphthenes as well as the removal of at least a portion of heteroatoms, hydrocracking wherein high boiling streams are converted to more valuable lower boiling streams, hydroisomerization wherein paraffinic compounds are converted to isoparaffins, hydrofinishing, which is a mild hydrotreating process used particularly to replace or supplement clay treating of lube oils and waxes. Other hydroprocessing process that are incorporated within this invention include catalytic dewaxing which is a catalytic hydrocracking process that uses molecular sieve catalysts to selectively hydrocrack waxes present in a feedstock into lighter hydrocarbon fractions; wax hydroisomerization wherein wax molecules are converted to branched molecules in a catalytic reaction and converted into high VI lubricants.

[0018] Also, lubricating and/or specialty oil stocks such as deasphalted oil stocks, lube oil distillates, and solvent extracted lube oil raffinates can have their viscosity indexes increased by hydrotreating, employing specific bulk metal sulfide hydrotreating catalysts selected from the group consisting of bulk Cr/Ni/Mo sulfide catalyst, bulk Ni/Mo/Mn sulfide catalyst and mixtures thereof wherein the catalysts are prepared from specific metal complexes and wherein the Ni/Mn/Mo sulfide catalyst is prepared from the oxide precursor decomposed in an inert atmosphere such as N₂ and subsequently sulfided using H₂S/H₂ and the Cr/Ni/Mo sulfide

catalyst is prepared from the sulfide precursor and decomposed in a non-oxidizing, sulfur containing atmosphere.

[0019] Herein, the term "hydrocarbon feed" is defined as a refinery, chemical or other industrial plant stream that is comprised of hydrocarbons including such streams wherein small levels (less than 5%) of non-hydrocarbon contaminants such as, but not limited to, sulfur, water, ammonia, and metals may be present in the hydrocarbon feed. The term "light hydrocarbons" means a hydrocarbon mixture comprised of hydrocarbon compounds of about 1 to about 5 carbon atoms in weight (i.e., C₁ to C₅ weight hydrocarbon compounds). It will be understood that the terms "hydrocarbon" and "hydrocarbonaceous" are used interchangeably herein when referring to feedstreams.

[0020] Feedstreams that can be hydroprocessed in accordance with the present invention are any hydrocarbonaceous feedstreams that are upgraded by hydroprocessing. Non-limiting examples of such feedstreams include light hydrocarbon boiling range feedstreams, naphtha boiling range feedstreams, kerosene and jet boiling range feedstreams, diesel and distillate boiling range feedstreams, cycle oils produced from the Fluid Catalytic Cracker (FCC), atmospheric and vacuum gas oils, atmospheric and vacuum residua, pyrolysis gasoline, Fischer-Tropsch liquids, raffinates, waxes, lube oils, and crudes, as well as heavier gas oil and resid boiling range feedstreams.

[0021] For example, in the case of hydrotreating, heteroatoms such as sulfur and nitrogen are typically removed from the aforementioned feed streams, whereas in the case of hydrocracking heavier boiling range gas oil and residue type streams are converted to lower boiling product streams. Non-limiting examples of naphtha feedstreams that can be treated in accordance with the present invention are those

containing components boiling in the range from about 50°F to about 450°F, at atmospheric pressure. The naphtha feedstream generally contains cracked naphtha which usually comprises fluid catalytic cracking unit naphtha (FCC catalytic naphtha), coker naphtha, hydrocracker naphtha, resid hydrotreater naphtha, debutanized natural gasoline (DNG), and gasoline blending components from other sources wherein a naphtha boiling range stream can be produced. Non-limiting examples of distillate feedstreams that can be treated in accordance with the present invention are those boiling in the range of about 288°C (550°F), such as atmospheric gas oils, vacuum gas oils, deasphalted vacuum and atmospheric residua, mildly cracked residual oils, coker distillates, straight run distillates, solvent-deasphalted oils, pyrolysis-derived oils, high boiling synthetic oils, cycle oils and cat cracker distillates. A preferred hydrotreating feedstock is a gas oil or other hydrocarbon fraction having at least 50% by weight, and most usually at least 75% by weight of its components boiling at temperatures between about 316°C (600°F) and 538°C (1000°F). Crude oils can also be feed in accordance with the present invention.

[0022] Illustrative hydrocarbon feedstreams that are upgraded by hydrocracking include those containing components boiling above about 260°C (500°F), such as Fischer-Tropsch liquids, atmospheric gas oils, vacuum gas oils, deasphalted, vacuum, and atmospheric residua, hydrotreated or mildly hydrocracked residual oils, coker distillates, straight run distillates, solvent-deasphalted oils, pyrolysis-derived oils, high boiling synthetic oils, cycle oils and cat cracker distillates. A preferred hydrocracking feedstream is a gas oil or other hydrocarbon fraction having at least 50% by weight, and most usually at least 75% by weight, of its components boiling at temperatures above the end point of the desired product. One of the most preferred gas oil feedstreams will contain hydrocarbon components that boil above 260°C (500°F), with best results being achieved with feeds containing at

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least 25 percent by volume of the components boiling between about 315°C (600°F) and 538°C (1000°F). A preferred heavy feedstream boils in the range from about 93°C to about 565°C (200-1050°F.). Hydroisomerization feedstreams are typically paraffinic, such as wax streams, particularly Fischer-Tropsch waxes and light paraffins.

[0023] The term "hydrotreating" as used herein refers to processes wherein a hydrogen-containing treat gas is used in the presence of suitable catalysts which are primarily active for the removal of heteroatoms, such as sulfur and nitrogen and for some hydrogenation of aromatics. Suitable hydrotreating catalysts for use in the present invention are any known conventional hydrotreating catalysts and include those which are comprised of at least one Group VIII metal, preferably iron, cobalt and nickel, more preferably cobalt and/or nickel and at least one Group VI metal, preferably molybdenum and tungsten, either as a bulk catalyst, or supported on a high surface area support material, preferably alumina. Other suitable hydrotreating catalysts include zeolitic catalysts, as well as noble metal catalysts where the noble metal is selected from palladium and platinum. It is within the scope of the present invention that more than one type of hydrotreating catalyst be used in the same reaction vessel. The Group VIII metal is typically present in an amount ranging from about 2 to about 20 wt. %, preferably from about 4 to about 12 wt. %. The Group VI metal will typically be present in an amount ranging from about 1 to about 25 wt.-%, preferably from about 2 to about 25 wt. %. As previously mentioned, typical hydrotreating temperatures range from about 204°C (400°F) to about 482°C (900°F) with pressures from about 3.5 MPa (500 psig) to about 17.3 MPa (2500 psig), preferably from about 3.5 MPa (500 psig) to about 13.8 MPa (2000 psig) and a liquid hourly space velocity of the feedstream from about 0.1 hr⁻¹ to about 10 hr⁻¹.

[0024] The active metals employed in the preferred hydrocracking catalysts of the present invention as hydrogenation components are those of Group VIII of the Periodic Table of the Elements, i.e., iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum. One or more promoter metals can also be present. Preferred promoter metals are those from Group VIB, e.g., molybdenum and tungsten, more preferably molybdenum. The amount of hydrogenation metal component in the catalyst can vary within wide ranges. Broadly speaking, any amount between about 0.05 percent and 30 percent by weight may be used. In the case of the noble metals, it is preferred to use about 0.05 to about 2 weight percent of such metals. The preferred method for incorporating the hydrogenation metal component is to contact a zeolite base material, preferably a zeolite with the Faujasite or Beta zeolite structure, with an aqueous solution of a suitable compound of the desired metal wherein the metal is present in a cationic form. Following addition of the selected hydrogenation metal or metals, the resulting catalyst powder is then filtered, dried, pelleted with added lubricants, binders or the like if desired, and calcined in air at temperatures of, e.g., 371° -648°C. (700°-1200°F.) in order to activate the catalyst and decompose ammonium ions. Alternatively, the zeolite component may first be pelleted, followed by the addition of the hydrogenating component and activation by calcining. The foregoing catalysts may be employed in undiluted form, or the powdered zeolite catalyst may be mixed and copelleted with other relatively less active catalysts, diluents or binders such as alumina, silica gel, silica-alumina cogels, activated clays and the like in proportions ranging between 5 and 90 weight percent. These diluents may be employed as such or they may contain a minor proportion of an added hydrogenating metal such as a Group VIB and/or Group VIII metal. Additional metal promoted hydrocracking catalysts may also be utilized in the process of the present invention which comprises, for example, aluminophosphate molecular sieves, crystalline chromosilicates and other

crystalline silicates. Crystalline chromosilicates are more fully described in U.S. Pat. No. 4,363,718 (Klotz).

[0025] Hydrocracking is typically performed at a temperature from about 232°C (450°F) to about 468°C (875°F), at a pressure from about 3.6 MPa (500 psig) to about 20.8 MPa (3000 psig), at a liquid hourly space velocity (LHSV) from about 0.1 to about 30 hr⁻¹, and at a hydrogen circulation rate from about 337 normal m³/m³ (2000 standard cubic feet per barrel) to about 4200 normal m³/m³ (25,000 standard cubic feet per barrel). In accordance with the present invention, the term "substantial conversion to lower boiling products" is meant to connote the conversion of at least 5 volume percent of the fresh feedstock to lower boiling products. In a preferred embodiment, the per pass conversion in the hydrocracking zone is in the range from about 15% to about 45%. More preferably the per pass conversion is in the range from about 20% to about 40%.

[0026] The hydroisomerization of the hydrocarbon feedstock is performed in a hydroisomerization zone which includes a hydroisomerization catalyst, the presence of hydrogen, and which is operated under hydroisomerization conditions sufficient to hydrogenate diolefins to mono-olefins and to isomerize mono-olefins. Preferably, the hydroisomerization conditions include a temperature in the range of from about 0° F to about 500°F, more preferably from about 75°F to about 400°F, and most preferably from 100°F to 200°F; a pressure in the range of from about 100 psig to about 1500 psig, more preferably from about 150 psig to about 1000 psig, and most preferably from 200 psig to 600 psig; and a liquid hourly space velocity (LHSV) in the range of from about 0.01 hr⁻¹ to about 100 hr⁻¹, more preferably from 1 hr⁻¹ to about 50 hr⁻¹, and most preferably from 5 hr⁻¹ to 15 hr⁻¹. Hydroisomerization of paraffinic hydrocarbons typically employs a catalyst composed of a noble metal, alumina and chlorine, said catalyst prepared by treating

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a composite of a noble metal and alumina with an inorganic or organic salt of aluminum, preferably aluminum nitrate, calcining the treated composite and thereafter contacting the composite with a conventional chloride activating agent.

[0027] Wax hydroisomerization is also an important process, especially when converting slack waxes as well as Fischer-Tropsch waxes to more valuable fuel and lube products have acceptable pour points with a high viscosity index. Waxes are typically hydroisomerized using a catalyst containing a hydrogenating metal component-typically one from Group IV, or Group VIII of the Periodic Table, or mixtures thereof. The reaction is conducted under conditions of temperature between about 500°F to 750°F, preferably between about 570°F to 680°F, and pressures of from about 500 to 3000 psi H₂ preferably from about 500-1500 psi H₂, at hydrogen gas rates from 1000 to 10,000 SCF/bbl, and at space velocities in the range of from 0.1 to 10 v/v/hr, preferably from 0.5 to 2 v/v/hr. Following hydroisomerization, the isomerate is fractionated into a lubes cut and a fuels cut. The lubes cut can then be dewaxed to recover unconverted wax.

[0028] In Conventional Pressure Swing Adsorption ("conventional PSA") a gaseous mixture is conducted under pressure for a period of time over a first bed of a solid sorbent that is selective or relatively selective for one or more components, usually regarded as a contaminant that is to be removed from the gas stream. It is possible to remove two or more contaminants simultaneously but for convenience, the component or components that are to be removed will be referred to in the singular and referred to as a contaminant. The gaseous mixture is passed over a first adsorption bed in a first vessel and emerges from the bed depleted in the contaminant that remains sorbed in the bed. After a predetermined time or, alternatively when a break-through of the contaminant is observed, the flow of the gaseous mixture is switched to a second adsorption bed in a second vessel for the

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purification to continue. While the second bed is in adsorption service, the sorbed contaminant is removed from the first adsorption bed by a reduction in pressure, usually accompanied by a reverse flow of gas to desorb the contaminant. As the pressure in the vessels is reduced, the contaminant previously adsorbed on the bed is progressively desorbed into the tail gas system that typically comprises a large tail gas drum, together with a control system designed to minimize pressure fluctuations to downstream systems. The contaminant can be collected from the tail gas system in any suitable manner and processed further or disposed of as appropriate. When desorption is complete, the sorbent bed may be purged with an inert gas stream, e.g., nitrogen or a purified stream of the process gas. Purging may be facilitated by the use of a higher temperature purge gas stream.

[0029] After, e.g., breakthrough in the second bed, and after the first bed has been regenerated so that it is again prepared for adsorption service, the flow of the gaseous mixture is switched from the second bed to the first bed, and the second bed is regenerated. The total cycle time is the length of time from when the gaseous mixture is first conducted to the first bed in a first cycle to the time when the gaseous mixture is first conducted to the first bed in the immediately succeeding cycle, i.e., after a single regeneration of the first bed. The use of third, fourth, fifth, etc. vessels in addition to the second vessel, as might be needed when adsorption time is short but desorption time is long, will serve to increase cycle time.

[0030] Thus, in one configuration, a pressure swing cycle will include a feed step, at least one depressurization step, a purge step, and finally a repressurization step to prepare the adsorbent material for reintroduction of the feed step. The sorption of the contaminants usually takes place by physical sorption onto the sorbent that is normally a porous solid such as alumina, silica or silica-alumina that

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has an affinity for the contaminant. Zeolites are often used in many applications since they may exhibit a significant degree of selectivity for certain contaminants by reason of their controlled and predictable pore sizes. Normally, chemical reaction with the sorbent is not favored in view of the increased difficulty of achieving desorption of species which have become chemically bound to the sorbent but chemisorption is by no means to be excluded if the sorbed materials may be effectively desorbed during the desorption portion of the cycle, e.g., by the use of higher temperatures coupled with the reduction in pressure.

[0031] Conventional PSA is not suitable for use in the present invention for a variety of reasons. For example, conventional PSA units are costly to build and operate and are much larger in size for the amount of hydrogen that needs to be recovered from such streams as compared to RCPSA. Also, a conventional pressure swing adsorption unit will generally have cycle times in excess of one minute, typically in excess of 2 to 4 minutes due to time limitations required to allow diffusion of the components through the larger beds utilized in conventional PSA and the equipment configuration and valving involved. Instead, rapid cycle pressure swing adsorption is utilized which has cycle times of less than one minute. The total cycle times may be less than 30 seconds, preferably less than 15 seconds, more preferably less than 10 seconds, even more preferably less than 5 seconds, and even more preferably less than 2 seconds. Further, the rapid cycle pressure swing adsorption units used can make use of substantially different sorbents, such as, but not limited to, structured materials such as monoliths.

[0032] The overall adsorption rate of the adsorption processes, whether conventional PSA or RCPSA, is characterized by the mass transfer rate constant in the gas phase (τ_g) and the mass transfer rate constant in the solid phase (τ_s). A material's mass transfer rates of a material are dependent upon the adsorbent, the

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adsorbed compound, the pressure and the temperature. The mass transfer rate constant in the gas phase is defined as:

$$\tau_g = D_g / R_g^2 \quad (\text{in cm}^2/\text{sec}) \quad (1)$$

where D_g is the diffusion coefficient in the gas phase and R_g is the characteristic dimension of the gas medium. Here the gas diffusion in the gas phase, D_g , is well known in the art and the characteristic dimension of the gas medium, R_g is defined as the channel width between two layers of the structured adsorbent material.

[0033] The mass transfer rate constant in the solid phase of a material is defined as:

$$\tau_s = D_s / R_s^2 \quad (\text{in cm}^2/\text{sec}) \quad (2)$$

where D_s is the diffusion coefficient in the solid phase and R_s is the characteristic dimension of the solid medium. Here the gas diffusion coefficient in the solid phase, D_s , is well known in the art and the characteristic dimension of the solid medium, R_s is defined as the width of the adsorbent layer.

[0034] D. M. Ruthven & C. Thaeron, *Performance of a Parallel Passage Absorbent Contactor*, Separation and Purification Technology 12 (1997) 43-60, which is incorporated by reference, clarifies that for flow through a monolith or a structured adsorbent that channel width is a good characteristic dimension for the gas medium, R_g . U.S. patent 6,607,584 to Moreau et al., which is incorporated by reference, also describes the details for calculating these transfer rates and associated coefficients for a given adsorbent and standard stream composition for conventional PSA. Calculation of these mass transfer rate constants is well known

to one of ordinary skill in the art and may also be derived by one of ordinary skill in the art from standard testing data.

[0035] Conventional PSA relies on the use of adsorbent beds of particulate adsorbents. Additionally, due to construction constraints, conventional PSA is usually comprised of 2 or more separate beds that cycle so that at least one or more beds is fully or at least partially in the feed portion of the cycle at any one time in order to limit disruptions or surges in the treated process flow. However, due to the relatively large size of conventional PSA equipment, the particle size of the adsorbent material is general limited particle sizes of about 1 mm and above. Otherwise, excessive pressure drop, increased cycle times, limited desorption, and channeling of feed materials will result.

[0036] RCPSA utilizes a rotary valving system to conduct the gas flow through a rotary sorber module that contains a number of separate compartments each of which is successively cycled through the sorption and desorption steps as the rotary module completes the cycle of operations. The rotary sorber module is normally comprised of tubes held between two seal plates on either end of the rotary sorber module wherein the seal plates are in contact with a stator comprised of separate manifolds wherein the inlet gas is conducted to the RCPSA tubes and processed purified product gas and the tail gas exiting the RCPSA tubes is conducted away from rotary sorber module. By suitable arrangement of the seal plates and manifolds, a number of individual compartments may be passing through the characteristic steps of the complete cycle at any one time. In contrast with conventional PSA, the flow and pressure variations required for the sorption/desorption cycle may be changed in a number of separate increments on the order of seconds per cycle, which smoothes out the pressure and flow rate pulsations encountered by the compression and valving machinery. In this form,

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the RCPSA module includes valving elements angularly spaced around the circular path taken by the rotating sorption module so that each compartment is successively passed to a gas flow path in the appropriate direction and pressure to achieve one of the incremental pressure/flow direction steps in the complete RCPSA cycle. A key advantage of the RCPSA technology is a much more efficient use of the adsorbent material. Since the quantity of adsorbent required with RCPSA technology can be only a fraction of that required for conventional PSA technology to achieve the same separation quantities and qualities. The footprint, investment, and the amount of active adsorbent required for RCPSA is significantly lower than that for a conventional PSA unit processing an equivalent amount of gas.

[0037] In an embodiment, RCPSA bed length unit pressure drops, required adsorption activities, and mechanical constraints (due to centrifugal acceleration of the rotating beds in RCPSA), prevent the use of many conventional PSA adsorbent bed materials, in particular adsorbents that are in a loose pelletized, particulate, beaded, or extrudate form. In a preferred embodiment, adsorbent materials are secured to a supporting understructure material for use in an RCPSA rotating apparatus. For example, one embodiment of the rotary RCPSA apparatus can be in the form of adsorbent sheets comprising adsorbent material coupled to a structured reinforcement material. A suitable binder may be used to attach the adsorbent material to the reinforcement material. Non-limiting examples of reinforcement material include monoliths, a mineral fiber matrix, (such as a glass fiber matrix), a metal wire matrix (such as a wire mesh screen), or a metal foil (such as aluminum foil), which can be anodized. Examples of glass fiber matrices include woven and non-woven glass fiber scrims. The adsorbent sheets can be made by coating a slurry of suitable adsorbent component, such as zeolite crystals with binder constituents onto the reinforcement material, such as nonwoven fiber glass scrims,

woven metal fabrics, and expanded aluminum foils. In a particular embodiment, adsorbent sheets or material are coated onto a ceramic support.

[0038] An absorber in a RCPSA unit typically comprises an adsorbent solid phase formed from one or more adsorbent materials and a permeable gas phase through which the gases to be separated flow from the inlet to the outlet of the adsorber, the components to be removed being fixed on the solid phase. This gas phase is called "circulating gas phase" or more simply "gas phase". The solid phase includes a network of pores, the mean size of which is usually between approximately 0.02 μm and 20 μm . There may be a network of even smaller pores, called "micropores", this being encountered, for example, in microporous carbon adsorbents or zeolites. As previously mentioned, the solid phase may be deposited on a non-adsorbent support, the function of which is to provide mechanical strength or support, or else to play a thermal conduction role or to store heat. The phenomenon of adsorption comprises two main steps, namely passage of the adsorbate from the circulating gas phase onto the surface of the solid phase, followed by passage of the adsorbate from the surface to the volume of the solid phase into the adsorption sites.

[0039] In an embodiment, RCPSA utilizes a structured adsorbent which is incorporated into tubes utilized in the RSPCA apparatus. These structured adsorbents have an unexpectedly high mass transfer rate since the gas flow is through the channels formed by the structured sheets of the adsorbent which offers a significant improvement in mass transfer as compared to a traditional packed fixed bed arrangement as utilized in conventional PSA. The ratio of the transfer rate of the gas phase (τ_g) and the mass transfer rate of the solid phase (τ_s) in the current invention is greater than 10, preferably greater than 25, more preferably greater than 50. These extraordinarily high mass transfer rate ratios allow RCPSA

to produce high purity hydrogen at a high recovery rate with only a fraction of the equipment size, adsorbent volume, and cost of conventional PSA.

[0040] The structured adsorbent embodiments also results in significantly greater pressure drops to be achieved through the adsorbent than conventional PSA without the detrimental effects associated with particulate bed technology. The adsorbent beds can be designed with adsorbent bed unit length pressure drops of greater than 5 inches of water per foot of bed length, more preferably greater than 10 in. H₂O/ft, and even more preferably greater than 20 in. H₂O/ft. This is in contrast with conventional PSA units where the adsorbent bed unit length pressure drops are generally limited to below about 5 in. H₂O/ft depending upon the adsorbent used, with most conventional PSA units being designed with a pressure drop of about 1 in. H₂O/ft or less to minimize the problems discussed that are associated with the larger beds, long cycle time, and particulate adsorbents of conventional PSA units. The adsorbent beds of conventional PSA cannot accommodate higher pressure drops because of the risk of fluidizing the beds which results in excessive attrition and premature unit shutdowns due to accompanying equipment problems and/or a need to add or replace lost adsorbent materials. These markedly higher adsorbent bed unit length pressure drops allow RCPSA adsorbent beds to be significantly more compact, shorter, and efficient than conventional PSA.

[0041] The achievement and accommodation of the high unit length pressure drops of the current embodiment allow high vapor velocities to be achieved across the structured adsorbent beds. This results in a greater mass contact rate between the process fluids and the adsorbent materials in a unit of time than can be achieved by conventional PSA. This results in shorter bed lengths, higher gas phase transfer rates (τ_p) and improved hydrogen recovery. With these significantly shorter bed

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lengths, total pressure drops of the RSCPA application of the present invention can be maintained at total bed pressure differentials during the feed cycle of about 10 to 50 psig, preferably less than 30 psig, while minimizing the active adsorbent beds to less than 5 feet in length, preferably less than 2 feet in length and as short as less than 1 foot in length.

[0042] The absolute pressure levels employed during the RCPSA process are not critical provided that the pressure differential between the adsorption and desorption steps is sufficient to cause a change in the adsorbate fraction loading on the adsorbent thereby providing a delta loading effective for separating the stream components processed by the RCPSA unit. Typical pressure levels range of the from about 50 to 2000 psia, more preferably from about 80 to 500 psia during the adsorption step. However, it should be noted that the actual pressures utilized during the feed, depressurization, purge and repressurization stages is highly dependent upon many factors including, but not limited to, the actual operating pressure and temperature of the overall stream to be separated, stream composition, and desired recovery percentage and purity of the RCPSA product stream. U.S. Patent Nos. 6,406,523; 6,451,095; 6,488,747; 6,533,846 and 6,565,635, all of which are incorporated herein by reference, disclose various aspects of RCPSA technology.

[0043] In an embodiment, the rapid cycle pressure swing adsorption system has a total cycle time, t_{TOT} , to separate a feed gas into product gas (in this case, a hydrogen-enriched stream) and a tail (exhaust) gas. The method generally includes the steps of conducting the feed gas having a hydrogen purity $F\%$, where F is the percentage of the feed gas which is the weakly-adsorbable (hydrogen) component, into an adsorbent bed that selectively adsorbs the tail gas and passes the hydrogen product gas out of the bed, for time, t_F , wherein the hydrogen product gas has a

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purity of P% and a rate of recovery of R%. Recovery R % is the ratio of amount of hydrogen retained in the product to the amount of hydrogen available in the feed. Then the bed is co-currently depressurized for a time, t_{CO} , followed by counter-currently depressurizing the bed for a time, t_{CN} , wherein desorbate (tail gas or exhaust gas) is released from the bed at a pressure greater than or equal to 30 psig. The bed is purged for a time, t_P , typically with a portion of the hydrogen product gas. Subsequently the bed is repressurized for a time, t_{RP} , typically with a portion of hydrogen product gas or feed gas, wherein the cycle time, t_{TOT} , is equal to the sum of the individual cycle times comprising the total cycle time, i.e.

$$t_{TOT} = t_F + t_{CO} + t_{CN} + t_P + t_{RP} \quad (3)$$

[0044] This embodiment encompasses, but is not limited to, RCPSA processes such that either the rate of recovery, $R\% > 80\%$ for a product purity to feed purity ratio, $P\%/F\% > 1.1$, and/or the rate of recovery, $R\% > 90\%$ for a product purity to feed purity ratio, $0 < P\%/F\% < 1.1$. Results supporting these high recovery & purity ranges can be found in Examples 4 through 10 below. Other embodiments will include applications of RCPSA in processes where recovery rates are much lower than 80%. Embodiments of RCPSA are not limited to exceeding any specific recovery rate or purity thresholds and can be as applied at recovery rates and/or purities as low as desired or economically justifiable for a particular application.

[0045] It should also be noted that it is within the scope of this invention that steps t_{CO} , t_{CN} , or t_P of equation (3) above can be omitted together or in any individual combination. However it is preferred that all steps in the above equation (3) be performed or that only one of steps t_{CO} or t_{CN} be omitted from the total cycle.

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[0046] In an embodiment, the tail gas is also preferably released at a pressure high enough so that the tail gas may be fed to another device absent tail gas compression. More preferably the tail gas pressure is greater than or equal to 60 psig. In a most preferred embodiment, the tail gas pressure is greater than or equal to 80 psig. At higher pressures, the tail gas can be conducted to a fuel header or directly to another process unit in a refinery or petrochemical, such as a hydroprocessing unit, a reforming unit, a fluidized catalytic cracker unit or a methane synthesis unit. It is also within the scope of this invention for this particular embodiment that the only step in depressuring the bed is co-current flow. That is, the counter-current depressurizing step is omitted.

[0047] Practice of the present invention can have the following benefits:

(a) Increasing the purity of hydrogen-containing stream(s) available as makeup gas, or of streams which must be upgraded to higher purity before they are suitable as make-up gas.

(b) Increasing the purity of hydrogen-containing recycle gas streams resulting in an increase in overall hydrogen treat gas purity in the reactor to allow for higher hydrotreating severity or additional product treating.

(c) Use for H₂ recovery from hydroprocessing purge gases, either where significant concentrations of H₂S are present (before gas scrubbing) or after gas scrubbing (typically <100 vppm H₂S).

[0048] In hydroprocessing, increased H₂ purity translates to higher H₂ partial pressures in the hydroprocessing reactor(s). This both increases the reaction kinetics and decreases the rate of catalyst deactivation. The benefits of higher H₂

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partial pressures can be exploited in a variety of ways, such as: operating at lower reactor temperature, which reduces energy costs, decreases catalyst deactivation, and extends catalyst life; increasing unit feed rate; processing more sour (higher sulfur) feedstocks; processing higher concentrations of cracked feedstocks; improved product color, particularly near end of run; debottlenecking existing compressors and/or treat gas circuits (increased scf H₂ at constant total flow, or same scf H₂ at lower total flow); and other means that would be apparent to one skilled in the art.

[0049] Increased H₂ recovery also offers significant potential benefits, some of which are described as follows:

- (i) reducing the demand for purchased, manufactured, or other sources of H₂ within the refinery;
- (ii) increasing hydroprocessing feed rates at constant (existing) makeup gas demands as a result of the increased hydrogen recovery;
- (iii) improving the hydrogen purity in hydroprocessing for increased heteroatom removal efficiencies;
- (iv) removing a portion of the H₂ from refinery fuel gas which is detrimental to the fuel gas due to hydrogen's low BTU value which can present combustion capacity limitations and difficulties for some furnace burners;
- (v) Other benefits that would be apparent to one knowledgeable in the art.

[0050] Depending on the specific RCPSA design, other contaminants, such as, but not limited to CO₂, water, and ammonia may also be removed from a feed. A portion of the scrubbed vapor stream may bypass the RCPSA unit.

[0051] The following examples are presented for illustrative purposes only and should not be cited as being limiting in any way.

EXAMPLES**Example 1**

[0052] In this example, the refinery stream is at 480 psig with tail gas at 65 psig whereby the pressure swing is 6.18. The feed composition and pressures are typical of refinery processing units such as those found in hydroprocessing or hydrotreating applications. In this example typical hydrocarbons are described by their carbon number i.e. C_1 = methane, C_2 = ethane etc. The RCPSA is capable of producing hydrogen at > 99 % purity and > 81 % recovery over a range of flow rates. Tables 1a and 1b show the results of computer simulation of the RCPSA and the input and output percentages of the different components for this example. Tables 1a and 1b also show how the hydrogen purity decreases as recovery is increased from 89.7 % to 91.7 % for a 6 MMSCFD stream at 480 psig and tail gas at 65 psig.

Tables 1a and 1b

Composition (mol %) of input and output from RCPSA (67 ft³) in H₂ purification. Feed is at 480 psig, 122 deg F and Tail gas at 65 psig. Feed rate is about 6 MMSCFD.

Table 1a - Higher purity

Step Times in seconds are $t_F = 1$, $t_{CO} = 0.167$, $t_{CN} = 0$, $t_P = 0.333$, $t_{RP} = 0.5$

H₂ at 98.6% purity, 89.7% recovery

	FEED	PRODUCT	TAIL-GAS
H ₂	88.0	98.69	45.8
C ₁	6.3	1.28	25.1
C ₂	0.2	0.01	1.0
C ₃	2.6	0.01	12.3
C ₄₊	2.9	0.00	14.8
H ₂ O	2000 vppm	65 vppm	9965 vppm
TOTAL (MMSCFD)	6.162	4.934	1.228
	480 psig	470 psig	65 psig

Table 1b - Higher purity

Step Times in seconds are $t_F = 1$, $t_{CO} = 0.333$, $t_{CN} = 0$, $t_P = 0.167$, $t_{RP} = 0.5$

H₂ at 97.8% purity, 91.7% recovery

	FEED	PRODUCT	TAIL-GAS
H ₂	88.0	97.8	45.9
C ₁	6.3	2.14	25.0
C ₂	0.2	0.02	1.0
C ₃	2.6	0.02	12.3
C ₄₊	2.9	0.00	14.9
H ₂ O	2000 vppm	131 vppm	10016 vpm
TOTAL (MMSCFD)	6.160	5.085	1.074
	480 psig	470 psig	65 psig

[0053] The RCPSA's described in the present invention operate a cycle consisting of different steps. Step 1 is feed during which product is produced, step 2 is co-current depressurization, step 3 is counter-current depressurization, step 4 is

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purge, usually counter-current) and step 5 is repressurization with product. In the RCPSA's described here at any instant half the total number of beds are on the feed step. In this example, $t_{TOT} = 2$ sec in which the feed time, t_F , is one-half of the total cycle.

Example 2

[0054] In this example, the conditions are the same as in Example 1. Table 2a shows conditions utilizing both a co-current and counter-current steps to achieve hydrogen purity > 99 %. Table 2b shows that the counter-current depressurization step may be eliminated, and a hydrogen purity of 99% can still be maintained. In fact, this shows that by increasing the time of the purge cycle, t_P , by the duration removed from the counter-current depressurization step, t_{CN} , that hydrogen recovery can be increased to a level of 88%.

Tables 2a and 2b

Effect of step durations on H₂ purity and recovery from an RCPSA (67 ft³). Same conditions as Table 1. Feed is at 480 psig, 122 deg F and Tail gas at 65 psig. Feed rate is about 6 MMSCFD.

Table 2a

With counter-current depress, Intermediate pressure = 105 psig.

Purity	Recovery	t_F	t_{CO}	t_{CN}	t_P	t_{RP}
%	%	s	S	s	S	S
98.2	84.3	1	0.283	0.05	0.167	0.5
98.3	85	1	0.166	0.167	0.167	0.5
99.9	80	1	0.083	0.25	0.167	0.5

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Table 2b**Without counter-current depress**

Purity	Recovery	t_F	t_{CO}	t_{CN}	t_P	t_{RP}
%	%	s	S	s	S	s
97.8	91.7	1	0.333	0	0.167	0.5
98.7	90	1	0.166	0	0.334	0.5
99	88	1	0.083	0	0.417	0.5

Example 3

[0055] This example shows a 10 MMSCFD refinery stream, once again containing typical components, as shown in feed column of Table 3 (e.g. the feed composition contains 74 % H_2). The stream is at 480 psig with RCPSA tail gas at 65 psig whereby the absolute pressure swing is 6.18. Once again the RCPSA of the present invention is capable of producing hydrogen at > 99 % purity and > 85 % recovery from these feed compositions. Tables 3a and 3b show the results of this example.

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Tables 3a and 3b

Composition (mol %) of input and output from RCPSA (53 ft³) in H₂ purification. Feed is at 480 psig, 101 deg F and Tail gas at 65 psig. Feed rate is about 10 MMSCFD.

Table 3a - Higher purity

Step Times in seconds are $t_F = 0.583$, $t_{CO} = 0.083$, $t_{CN} = 0$, $t_P = 0.25$, $t_{RP} = 0.25$

H₂ at 99.98 % purity and 86 % recovery

	FEED	PRODUCT	TAIL-GAS
H ₂	74.0	99.98	29.8
C ₁	14.3	0.02	37.6
C ₂	5.2	0.00	13.8
C ₃	2.6	0.00	7.4
C ₄₊	3.9	0.00	11.0
H ₂ O	2000 vppm	0.3 vppm	5387 vppm
TOTAL (MMSCFD)	10.220	6.514	3.705
	480 psig	470 psig	65 psig

Table 3b - Lower purity

Step Times in seconds are $t_F = 0.5$, $t_{CO} = 0.167$, $t_{CN} = 0$, $t_P = 0.083$, $t_{RP} = 0.25$

H₂ at 93 % purity and 89 % recovery

	FEED	PRODUCT	TAIL-GAS
H ₂	74.0	93.12	29.3
C ₁	14.3	6.34	31.0
C ₂	5.2	0.50	16.6
C ₃	2.6	0.02	8.9
C ₄₊	3.9	0.00	13.4
H ₂ O	2000 vppm	142 vppm	6501 vppm
TOTAL (MMSCFD)	10.220	7.240	2.977
	480 psig	470 psig	65 psig

[0056] In both cases shown in Tables 3a and 3b above, although tail gas pressure is high at 65 psig, the present invention shows that high purity (99 %) may be obtained if the purge step, t_P , is sufficiently increased.

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[0057] Tables 2a, 2b and 3a show that for both 6 MMSCFD and 10 MMSCFD flow rate conditions, very high purity hydrogen at ~99 % and > 85 % recovery is achievable with the RCPSA. In both cases the tail gas is at 65 psig. Such high purities and recoveries of product gas achieved using the RCPSA with all the exhaust produced at high pressure have not been discovered before and are a key feature of the present invention.

[0058] Table 3c shows the results for an RCPSA (volume = 49 cubic ft) that delivers high purity (> 99%) H₂ at high recovery for the same refinery stream discussed in Tables 3a and 3b. As compared to Table 3a, Table 3c shows that similar purity and recovery rates can be achieved by simultaneously decreasing the duration of the feed cycle, t_F , and the purge cycle, t_P .

Table 3c

Effect of step durations on H₂ purity and recovery from an RCPSA (49 ft³). Feed is at 480 psig, 101 deg F and Tail gas at 65 psig. Feed rate is about 10 MMSCFD.

Without counter-current depress.

Purity	Recovery	t_F	t_{CO}	t_{CN}	t_P	t_{RP}
%	%	s	S	S	s	s
95.6	87.7	0.5	0.167	0	0.083	0.25
97.6	86	0.5	0.117	0	0.133	0.25
99.7	85.9	0.5	0.083	0	0.167	0.25

Example 4

[0059] In this example, Table 4 further illustrates the performance of RCPSA's operated in accordance with the invention being described here. In this example, the feed is a typical refinery stream and is at a pressure of 300 psig. The RCPSA of the present invention is able to produce 99 % pure hydrogen product at 83.6 % recovery when all the tail gas is exhausted at 40 psig. In this case the tail gas can be sent to a flash drum or other separator or other downstream refinery equipment without further compression requirement. Another important aspect of this invention is that the RCPSA also removes CO to < 2 vppm, which is extremely desirable for refinery units that use the product hydrogen enriched stream. Lower levels of CO ensure that the catalysts in the downstream units operate without deterioration in activity over extended lengths. Conventional PSA cannot meet this CO specification and simultaneously also meet the condition of exhausting all the tail gas at the higher pressure, such as at typical fuel header pressure or the high pressure of other equipment that processes such RCPSA exhaust. Since all the tail gas is available at 40 psig or greater, no additional compression is required for integrating the RCPSA with refinery equipment.

Table 4

Composition (mol %) of input and output from RCPSA (4 ft³) in carbon monoxide and hydrocarbon removal from hydrogen. Feed is at 300 psig, 101 deg F, and Feed rate is about 0.97 MMSCFD.

Step Times in seconds are $t_F = 0.5$, $t_{CO} = 0.1$, $t_{CN} = 0$, $t_P = 0.033$, $t_{RP} = 0.066$

H2 at 99.99 % purity and 88 % recovery

	FEED	PRODUCT	TAIL-GAS
H2	89.2	99.98	48.8
C1	3.3	0.01	13.9
C2	2.8	0.01	13.9
C3	2.0	0.00	10.2
C4+	2.6	0.00	13.2
CO	50	1.1	198.4
TOTAL	0.971	0.760	0.211
	300 psig	290 psig	40 psig

Example 5

[0060] Tables 5a and 5b compare the performance of RCPSA's operated in accordance with the invention being described here. The stream being purified has lower H₂ in the feed (51% mol) and is a typical refinery/petrochemical stream. In both cases (corresponding to Tables 5a and 5b), a counter current depressurization step is applied after the co-current step. In accordance with the invention, Table 5a shows that high H₂ recovery (81%) is possible even when all the tail gas is released at 65 psig or greater. In contrast, the RCPSA where some tail-gas is available as low as 5 psig, loses hydrogen in the counter-current depressurization such that H₂ recovery drops to 56%. In addition, the higher pressure of the stream in Table 5a indicates that no tail gas compression is required.

Tables 5a and 5b

Effect of Tail Gas Pressure on recovery. Example of RCPSA applied to a feed with H₂ concentration (51.3 mol %). Composition (mol %) of input and output from RCPSA (31 ft³) in H₂ purification. Feed is at 273 psig, 122 deg F and Feed rate is about 5.1 MMSCFD.

Table 5a

**Step Times in seconds are $t_F = 0.5$, $t_{CO} = 0.083$,
 $t_{CN} = 0.033$, $t_P = 0.25$, $t_{RP} = 0.133$**

[A] Tail gas available from 65-83 psig, H₂ at 99.7% purity and 81% recovery

	FEED	PRODUCT	TAIL-GAS
H ₂	51.3	99.71	20.1
C ₁	38.0	0.29	61.0
C ₂	4.8	0.00	8.0
C ₃	2.2	0.00	3.8
C ₄₊	3.7	0.00	6.4
H ₂ O	4000 vppm	0.7 vppm	6643 vppm
TOTAL (MMSCFD)	5.142	2.141	3.001
	273 psig	263 psig	65-83 psig

Table 5b

Step Times in sec. are $t_F = 0.667$, $t_{CO} = 0.167$, $t_{CN} = 0.083$, $t_P = 0.083$, $t_{RP} = 0.33$

[B] Tail gas available from 5-65 psig, H₂ at 99.9 % purity and 56 % recovery

	FEED	PRODUCT	TAIL-GAS
H ₂	51.3	99.99	34.2
C ₁	38.0	0.01	48.8
C ₂	4.8	0.00	6.9
C ₃	2.2	0.00	3.4
C ₄₊	3.7	0.00	6.2
H ₂ O	4000 vppm	0.0 vppm	5630 vppm
TOTAL (MMSCFD)	5.142	1.490	3.651
	273 psig	263 psig	5-65 psig

Example 6

[0061] In this example, Tables 6a and 6b compare the performance of RCPSA's operated in accordance with the invention being described here. In these cases, the feed pressure is 800 psig and tail gas is exhausted at either 65 psig or at 100 psig. The composition reflects typical impurities such H₂S, which can be present in such refinery applications. As can be seen, high recovery (> 80%) is observed in both cases with the high purity > 99 %. In both these cases, only a co-current depressurization is used and the effluent during this step is sent to other beds in the cycle. Tail gas only issues during the countercurrent purge step. Table 6c shows the case for an RCPSA operated where some of the tail gas is also exhausted in a countercurrent depressurization step following a co-current depressurization. The effluent of the co-current depressurization is of sufficient purity and pressure to be able to return it one of the other beds in the RCPSA vessel configuration that is part of this invention. Tail gas i.e., exhaust gas, issues during the counter-current depressurization and the counter-current purge steps.

[0062] In all cases the entire amount of tail gas is available at elevated pressure which allows for integration with other high pressure refinery process. This removes the need for any form of required compression while producing high purity gas at high recoveries. In accordance with the broad claims of this invention, these cases are only to be considered as illustrative examples and not limiting either to the refinery, petrochemical or processing location or even to the nature of the particular molecules being separated.

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Tables 6a, 6b, and 6c

Example of RCPSA applied to a high pressure feed. Composition (mol %) of input and output from RCPSA (18 ft³) in H₂ purification. Feed is at 800 psig, 122 deg F and Feed rate is about 10.1 MMSCFD.

Table 6a

Step Times in seconds are $t_F = 0.91$, $t_{CO} = 0.25$, $t_{CN} = 0$, $t_P = 0.33$, $t_{RP} = 0.33$

[A] Tail gas at 65 psig, H₂ at 99.9% purity and 87% recovery

	FEED	PRODUCT	TAIL-GAS
H ₂	74.0	99.99	29.5
C ₁	14.3	0.01	37.6
C ₂	5.2	0.00	14.0
C ₃	2.6	0.00	7.4
C ₄₊	3.9	0.00	10.9
H ₂ O	20 vppm	0	55 vppm
TOTAL (MMSCFD)	10.187	6.524	3.663
	800 psig	790 psig	65 psig

Table 6b

Step Times in seconds are $t_F = 0.91$, $t_{CO} = 0.25$, $t_{CN} = 0$, $t_P = 0.33$, $t_{RP} = 0.33$

[B] Tail gas at 100 psig, H₂ at 99.93% purity and 80.3% recovery

	FEED	PRODUCT	TAIL-GAS
H ₂	74.0	99.93	38.1
C ₁	14.3	0.07	32.8
C ₂	5.2	0.00	12.5
C ₃	2.6	0.00	6.5
C ₄₊	3.9	0.00	9.6
H ₂ S	20 vppm	0 vppm	49 vppm
TOTAL (MMSCFD)	10.187	6.062	4.125
	800 psig	790 psig	100 psig

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Table 6c

Step times in seconds are $t_F = 0.91$, $t_{CO} = 0.083$, $t_{CN} = 0.25$, $t_P = 0.167$, $t_{RP} = 0.41$

[C] Tail gas at 65-100 psig, H₂ at 99.8% purity and 84% recovery

	FEED	PRODUCT	TAIL-GAS
H ₂	74.0	99.95	28.9
C ₁	14.3	0.05	39.0
C ₂	5.2	0.00	13.7
C ₃	2.6	0.00	7.2
C ₄₊	3.9	0.00	10.6
H ₂ S	20 vppm	0.01 vppm	53 vppm
TOTAL (MMSCFD)	10.187	6.373	3.814
	800 psig	790 psig	65-100 psig

Example 7

[0063] Tables 7a, 7b, and 7c compare the performance of RCPSA's operated in accordance with the invention being described here. The stream being purified has higher H₂ in the feed (85 % mol) and is a typical refinery/petrochemical stream. In these examples the purity increase in product is below 10 % (i.e. $P/F < 1.1$). Under this constraint, the method of the present invention is able to produce hydrogen at > 90% recovery without the need for tail gas compression.

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Tables 7a, 7b, and 7c

Example of RCPSA applied to a Feed with H₂ concentration (85 mol %) .
Composition (mol %) of input and output from RCPSA (6.1 ft³). Feed is at
480 psig, 135 deg F and Feed rate is about 6 MMSCFD.

Table 7a

Step Times in seconds are $t_F = 0.5$, $t_{CO} = 0.33$, $t_{CN} = 0.167$, $t_P = 0.167$, $t_{RP} = 1.83$
recovery = 85 %

	FEED	PRODUCT	TAIL-GAS
H ₂	85.0	92.40	57.9
C ₁	8.0	4.56	17.9
C ₂	4.0	1.79	13.1
C ₃	3.0	1.16	10.4
C ₄₊	0.0	0.00	0.0
H ₂ O	2000	866.5	6915
TOTAL (MMSCFD)	6.100	4.780	1.320
	480 psig	470 psig	65 psig

Table 7b

Step Times in sec. are $t_F = 1$, $t_{CO} = 0.333$, $t_{CN} = 0.167$, $t_P = 0.083$, $t_{RP} = 0.417$
recovery = 90 %

	FEED	PRODUCT	TAIL-GAS
H ₂	85.0	90.90	58.2
C ₁	8.0	5.47	18.1
C ₂	4.0	2.23	12.9
C ₃	3.0	1.29	10.1
C ₄₊	0.0	0.00	0.0
H ₂ O	2000	1070.5	6823
TOTAL (MMSCFD)	6.120	5.150	0.969
	480 psig	470 psig	65 psig

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Table 7c

Step Times in sec. are $t_F=2$, $t_{CO}=0.667$, $t_{CN}=0.333$, $t_P=0.167$, $t_{RP}=0.833$
recovery = 90 %

	FEED	PRODUCT	TAIL-GAS
H2	85.0	90.19	55.2
C1	8.0	6.21	18.8
C2	4.0	2.32	13.9
C3	3.0	1.17	11.3
C4+	0.0	0.00	0.0
H2O	2000	1103.5	7447
TOTAL (MMSCFD)	6.138	5.208	0.93
	480 psig	470 psig	65 psig

CLAIMS

1. A process for upgrading a hydrocarbon feed in a hydroprocessing process unit, comprising:

a) contacting said hydrocarbon feed in a hydroprocessing zone with hydrogen, a portion of which is obtained from a hydrogen-containing make-up gas, and a catalytically effective amount of a hydroprocessing catalyst at hydroprocessing conditions thereby resulting in a liquid phase and a vapour phase;

b) separating said liquid phase product and said vapour phase, which vapour phase product contains hydrogen and light hydrocarbons;

c) removing at least a portion of the light hydrocarbons from the hydrogen-containing make-up treat gas, the vapour phase product, or both, in a rapid cycle pressure swing adsorption unit containing a plurality of adsorbent beds and having a total cycle time of less than about 30 seconds and a pressure drop within each adsorbent bed of greater than about 5 inches of water per foot of bed length;

d) recycling at least a portion of the vapour phase of step c) above having a higher concentration of hydrogen to the hydroprocessing zone,

wherein said vapor phase comprises (i) at least 6.3 mol% C1 hydrocarbons and at least 2.6 mol% C4+ hydrocarbons, (ii) at least 2000 vppm water, or (iii) both (i) and (ii), and wherein the purified hydrogen-containing gas stream is recovered from the rapid cycle pressure swing adsorption zone, relative to the vapor phase intermediate gas stream, so as to exhibit (iv) a rate of recovery (R%) greater than 80% for a product purity to feed ratio (P%/F%) greater than 1.1, (v) a rate of recovery (R%) greater than 90% for a product purity to feed ratio (P%/F%) less than 1.1 but greater than 0, or (vi) both (iv) and (v).

2. The process of claim 1 wherein the hydrocarbon feed is selected from the group consisting of naphtha boiling range feeds, kerosene and jet fuel boiling range feeds, distillate boiling range feeds, residues and crudes.

3. The process of claim 2 wherein the hydrocarbon feed is a naphtha boiling range feed selected from the group consisting of straight run naphtha, cat cracked naphtha, coker naphtha, hydrocracker naphtha, resid hydrotreater naphtha.

4. The process of claim 2 wherein the hydrocarbon feed is a distillate and higher boiling range feed selected from the group consisting of cycle oils produced from the Fluid Catalytic Cracker (FCC), atmospheric and vacuum gas oils, atmospheric and vacuum residua, pyrolysis gasoline, Fischer-Tropsch liquids, raffinates, waxes, lube oils, and crudes.

5. The process of claim 1 wherein the hydroprocessing processing is a hydrotreating process for the removal of heteroatoms from the hydrocarbon feed and wherein hydrogen sulfide is also a component of the vapor phase and wherein at least a portion of the hydrogen sulfide is removed in an acid gas scrubbing zone prior to having light hydrocarbons removed by rapid cycle pressure swing adsorption.

6. The process of claim 1 wherein the cycle time is less than about 10 seconds and the pressure drop is greater than about 10 inches of water per foot of bed length.

7. The process of claim 6 wherein the cycle time is less than about 5 seconds and the pressure drop is greater than about 20 inches of water per foot of bed length.

8. The process of claim 1 wherein the hydroprocessing process is hydrocracking wherein a hydrocarbon feed is converted to lower boiling products.

9. The process of claim 1 wherein the hydroprocessing process is hydroisomerization wherein molecules of the hydrocarbon feed are isomerized.

10. The process of claim 1 wherein the hydroprocessing process is hydrogenation wherein unsaturates and aromatics are hydrogenated.

11. The process of any one of claims 5, 8, 9 or 10 wherein the total cycle time or rapid cycle pressure swing adsorption is less than about 15 seconds.

12. The process of claim 11 wherein the total cycle time is less than about 10 seconds and the pressure drop of each adsorbent bed is greater than about 10 inches of water per foot of bed length.
- 5 13. The process of claim 12 wherein the total cycle time is less than about 5 seconds.
14. The process of claim 12 wherein the pressure drop is greater than about 20 inches of water per foot of bed length.
- 10 15. The process of claim 1 wherein said vapor phase further comprises (vii) no more than 38.0 mol% C1 hydrocarbons and no more than 3.9 mol% C4+ hydrocarbons, (viii) no more than 4000 vppm water, or (ix) both (vii) and (viii).