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(71) Applicant (for all designated States except US):
RUDOLF W. GUNNERMAN and PETER W. GUNNERMAN [US/US]; 6601 Windy Hill Way, Reno, NV 89511 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): GUNNERMAN, Rudolf, W. [US/US]; 6601 Windy Hill Way, Reno, NV 89511 (US). GUNNERMAN, Peter, W. [US/US]; 2630 Lakeridge Shores West, Reno, NV 89519 (US).

(74) Agents: HEINES, M., Henry et al.; Townsend And Townsend And Crew Llp, Two Embarcadero Center, 8th Floor, San Francisco, CA 94111-3834 (US).

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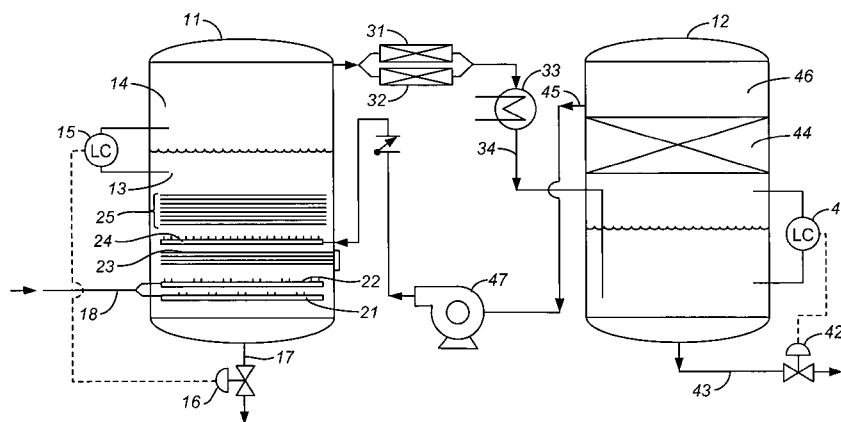


FIGURE 1

(57) Abstract: Biogases such as natural gas and other gases capable of being biologically derived by digestion of organic matter are converted to a clean-burning hydrocarbon liquid fuel in a process wherein a biogas is fed to a reaction vessel where the biogas contacts a liquid petroleum fraction and a transition metal catalyst immersed in the liquid, vaporized product gas is drawn from a vapor space above the liquid level, condensed, and fed to a product vessel where condensate is separated from uncondensed gas and drawn off as the liquid product fuel. Uncondensed gas can be recycled to the reaction vessel.

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PROCESS FOR CONVERSION OF BIOGAS TO LIQUID FUEL

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 [0001] This invention lies in the field of biogas and its use as a source of energy and its conversion to liquid fuel.

2. Description of the Prior Art

[0002] Alternative sources of energy are in ever increasing demand as crude oil fluctuates in price and as governments and the public at large become increasingly concerned over adverse
10 environmental impacts of gaseous emissions from the processing of crude oil. A major group of alternatives to crude oil are the gases commonly known as "biogas" which refers generally to gases resulting from the decomposition of organic matter in the absence of oxygen. The decomposition can occur in disposal facilities for treating municipal waste and waste products in general, and the decomposition processes generally include anaerobic digestion and fermentation
15 of biodegradable materials such as biomass, manure, sewage, municipal waste, and energy crops. The decomposition can also occur naturally in geological formations. Depending on its source, biogas can include hydrogen, methane, and carbon monoxide, as well as relatively benign gases such as nitrogen and carbon dioxide. Natural gas is one form of biogas.

SUMMARY OF THE INVENTION

20 [0003] It has now been discovered that biogas can be converted to a clean-burning liquid fuel that can drive an engine or any other machinery or appliance that is typically run by a petroleum-based fuel. The term "clean-burning" when used to describe a liquid fuel means a liquid fuel that

upon combustion produces a gaseous combustion product that is at least substantially free of particulate emissions and odor. The conversion of biogas to such a fuel in accordance with this invention is achieved by passing the biogas through a liquid reaction medium that contains a petroleum fraction, and doing so at an elevated but non-boiling temperature, while contacting the reaction medium with a transition metal catalyst. The gaseous product that results from the contact contains a vapor that can be condensed to achieve the liquid fuel. When the process is operated on a continuous basis, the product is produced in a volume that far exceeds the starting volume of the reaction medium.

[0004] A preferred design for a chemical plant in which the process of this invention is performed is one that includes a gas-liquid reaction vessel and a product vessel, with a gas feed to the reaction vessel for inlet biogas and a port on the product vessel from which to draw liquid product. Fluid transfer conduits connect the two vessels, including one such conduit transferring vaporized product from the reaction vessel through a condenser and then to the product vessel, and another such conduit transferring uncondensed gas from the product vessel back to the reaction vessel. Mounted inside the reaction vessel are a grid of transition metal catalyst and gas distributors for both the feed gas and the recycle gas, both under the liquid level. Optional features include a supplementary gas-phase reaction vessel downstream of the gas-liquid reaction vessel and upstream of the condenser, the supplementary vessel itself containing a grid of transition metal catalyst to react unreacted materials in the stream of vaporized product emerging from the reaction vessel. Further features of the plant design are described below.

[0005] The reaction medium in the gas-liquid reaction vessel is a liquid petroleum fraction, and the liquid product emerging from the product vessel is a hydrocarbon fuel of a composition that is distinct from the liquid petroleum fraction. The plant is operated on a continuous basis, and the reaction can be performed for a prolonged period of time, continuously producing product without adding further quantities of liquid petroleum fraction to the reaction vessel, although such further quantities can be added as needed to supplement the liquid level or compensate for liquid that has been entrained with the vaporized product. In either case, the product is readily produced in a volume that far exceeds the starting volume of the liquid petroleum fraction.

[0006] These and other objects, advantages, and features of the invention are included in the descriptions below.

BRIEF DESCRIPTION OF THE DRAWING

[0007] The Figure is a process flow diagram embodying an example of an implementation of
5 the invention.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

[0008] The term "biogas" is used herein to include any non-inert gas that can be produced by the biological degradation of organic matter. As noted above, prime examples of biogas are
10 hydrogen, methane, and carbon monoxide, although other gaseous petroleum-based products such as ethane and ethylene, and decomposition products of agricultural waste such as wood chips, grains, grasses, leaves, and the like, are likewise included within the scope of the term. The term is also used herein to include the same gases that are obtained from other sources. One example is methane associated with coal, commonly known as "coal bed methane," "coal mine
15 methane," and "abandoned mine methane." Such methane can be derived by bacterial activity or by heating. Gases containing 90% to 100% methane on a mole percent basis are of particular interest, and this includes natural gas, of which methane typically constitutes approximately 95 mole percent.

[0009] The petroleum fraction in the liquid reaction medium in the process of this invention
20 includes fossil fuels, crude oil fractions, and many of the components derived from these sources. The fossil fuels include any carbonaceous liquids that are derived from petroleum, coal, or any other naturally occurring material, as well as processed fuels such as gas oils and products of fluid catalytic cracking units, hydrocracking units, thermal cracking units, and cokers. Included among these fuels are automotive fuels such as gasoline, diesel fuel, jet fuel, and rocket
25 fuel, as well as petroleum residuum-based fuel oils including bunker fuels and residual fuels. Fractions or products in the diesel range can also be used, such as straight-run diesel fuel, feed-rack diesel fuel (diesel fuel that is commercially available to consumers at gasoline stations), light cycle oil, and blends of straight-run diesel and light cycle oil. Crude oil fractions include

any of the various refinery products produced from crude oil, either by atmospheric distillation or by vacuum distillation, as well as fractions that have been treated by hydrocracking, catalytic cracking, thermal cracking, or coking, and those that have been desulfurized. Examples of such fractions are light straight-run naphtha, heavy straight-run naphtha, light steam-cracked naphtha, 5 light thermally cracked naphtha, light catalytically cracked naphtha, heavy thermally cracked naphtha, reformed naphtha, alkylate naphtha, kerosene, hydrotreated kerosene, gasoline and light straight-run gasoline, straight-run diesel, atmospheric gas oil, light vacuum gas oil, heavy vacuum gas oil, residuum, vacuum residuum, light coker gasoline, coker distillate, FCC (fluid catalytic cracker) cycle oil, and FCC slurry oil. Preferred reaction media are mineral oil, diesel 10 oil, naphtha, kerosene, gas oil, and gasoline.

[0010] The transition metal catalyst can be any single transition metal or combination of transition metals, either as metal salts, pure metals, or metal alloys, and can also be used in combination with metals other than transition metals. Preferred catalysts for use in this invention are metals and metal alloys. Transition metals having atomic numbers ranging from 23 to 79 are 15 preferred, and those with atomic numbers ranging from 24 to 74 are more preferred. Cobalt, nickel, tungsten, and iron, particularly in combination, are the most preferred. An example of an additional metal that can be included is aluminum.

[0011] The metallic catalyst is used in solid form and is preferably maintained below the liquid level in the reaction vessel as the biogas is bubbled through the liquid and through or past the 20 catalyst. The catalyst can assume any form that allows intimate contact with both the liquid petroleum fraction and the biogas and allows free flow of gas over and past the catalyst. Examples of suitable forms of the catalyst are pellets, granules, wires, mesh screens, perforated plates, rods, and strips. Granules and wires suspended across plates or between mesh matrices such as steel or iron wool are preferred for their relatively accessible high surface area. When 25 granules are used, the granules can be maintained in a fluidized state in the reaction medium or held stationary in the form of a fixed bed. When wires are used, individual cobalt, nickel, aluminum, and tungsten wires, for example, of approximately equal diameter and length, and be strung across a frame of cast iron to form an open-mesh network which can then be supported inside the reactor. A reactor can contain a single frame strung with wires in this manner or two 30 or more such frames, depending on the size of the reactor. A still further variation of the catalyst

configuration that can be used is a coil or other wrapping of the metallic wire around or over piping that serves as a gas distributor for incoming gas. As mentioned above in the “SUMMARY OF THE INVENTION,” the reaction vessel will typically contain one or more gas distributors for incoming gas, and in certain embodiments of the invention as explained below, the distributor(s) may have a wheel-and-spokes configuration or any other shape that includes a network of hollow pipes with an array of apertures to form the gas into small bubbles for release into the reaction vessel. These pipes, or at least the apertures, can be covered for example with a steel mesh or steel wool in combination with wires of the various metals listed above, to intercept the gas bubbles before they enter the reaction medium. The term “metallic grid” is used herein to denote any fixed form of metallic catalyst that is submerged in the reaction medium and allows gas to bubble through the grid. The term thus encompasses fixed (as opposed to fluidized) beds, screens, open-weave wire networks, and any other forms described above. The metal can be in bare form or supported on inert supports as ceramic coatings or laminae.

[0012] The reaction is performed under non-boiling conditions to maintain the liquid petroleum fraction used as the reaction medium in a liquid state and to avoid or at least minimize the amount of the liquid that is vaporized and leaves the reaction vessel with the product. An elevated temperature, *i.e.*, one above ambient temperature, is used, preferably one that is about 80°C or above, more preferably one within the range of about 100°C to about 250°C. In certain embodiments, the most preferred temperature range is about 100°C to about 150°C, and in certain other embodiments, the most preferred temperature range is about 150°C to about 200°C. The operating pressure can vary as well, and can be either atmospheric, below atmospheric, or above atmospheric. The process is readily and most conveniently performed at either atmospheric pressure or a pressure moderately above atmospheric. Preferred operating pressures are those within the range of 1 atmosphere to 2 atmospheres.

[0013] The supplementary gas-phase reaction vessel referenced above as an optional feature of the invention is a flow-through vessel with a grid of metallic catalyst, in which the term “grid” has the same scope of meaning as stated above in connection with the gas-liquid reaction vessel. In the supplementary vessel, however, the grid is not submerged in a liquid but instead supported within the vessel in the path of the vaporized product emerging from the gas-liquid reaction

vessel. The metals in the grid can be the same as those in the grid of the gas-liquid reaction vessel, or different combinations of transition metals.

5 [0014] A process flow diagram representing one example of a plant design for implementation of the present invention is presented in the attached Figure. The reaction vessel **11** and the product vessel **12** are both shown. Each of these vessels is a closed cylindrical tank with a volumetric capacity of 2,000 gallons (U.S.) (7,570 cubic meters). The reaction vessel **11** is charged with a petroleum fraction used as a liquid reaction medium **13** with a gaseous head space **14** above the liquid. The liquid level is maintained by a level control **15** which is actuated by a pair of float valves inside the vessel. The level control **15** governs a motor valve **16** on a drain
10 line **17** at the base of the vessel.

[0015] Biogas is fed to the reaction vessel **11** underneath the liquid level at an inlet gas pressure of from about 5 psig to about 20 psig, through a gas inlet line **18** which is divided among two gas distributors **21**, **22** inside the reactor vessel, each distributor being large enough to deliver 1,000 scfm of gas to the vessel. Each distributor spans substantially the full cross
15 section of the vessel in either a grid configuration, a wheel-and-spokes configuration, or any other configuration that will support an array of outlet ports distributed across the cross section of the vessel. While two distributors are shown, the optimal number of distributors and outlet ports and the optimal configuration for any individual distributor will be readily determinable by routine experimentation, with greater or lesser numbers of distributors being optimal for reactor
20 vessels of different capacities. A resistance heater **23** is positioned in the reactor above the gas distributors, and a third gas distributor **24** is positioned above the resistance heater. The third gas distributor **24** receives return gas from the product receiving vessel **12** as explained below. The resistance heater **23** maintains the liquid at a temperature of approximately 240-250°F (116-121°C).

25 [0016] Positioned above the three gas distributors **21**, **22**, **24** and the resistance heater **23** but still beneath the liquid level are a series of catalyst grids **25** arranged in a stack. Each grid is a circular ring or apertured plate with metallic catalyst wires strung across the ring and supported by pegs affixed to the ring along the ring periphery. Of the variety of metals that can be used for the ring and the pegs, one example is a cast iron ring and chromium pegs. The sizes of the wires
30 and the total length of each wire will be selected to achieve the maximal surface area exposed to

the reaction medium while allowing gas to bubble through, and will be readily apparent to anyone skilled in the use of metallic or other solid-phase catalysts in a liquid-phase or gas-phase reaction. One example of a wire size is 1 mm in diameter. Using individual wires of each of four metals, such as for example cobalt, nickel, aluminum, and tungsten, two pounds of each metal wire can be used per ring, or eight pounds total per ring. The number of rings can vary, and will in most cases be limited only by the size of the reactor, the gas flow rate into the reactor, the desirability of maintaining little or minimal pressure drop across the rings, and economic factors such as the cost of materials. In a preferred embodiment, seven rings are used, each wound with the same number and weight of wires. The reaction can also be enhanced by placing screens of wire mesh between adjacent plates to assure that the gas bubbles contacting the catalyst wires are of a small size. Screens that are 40-mesh (U.S. Sieve Series) of either stainless steel or aluminum will serve this purpose.

[0017] Product gas is drawn from the head space **14** of the reaction vessel **11** and passed through a supplementary catalyst bed of the same catalyst material as the catalyst rings **25** of the reaction vessel. In the diagram shown, two such catalyst beds **31**, **32** of identical construction and catalyst composition are arranged in parallel. The supplementary catalyst can be in the form of metallic wire screens, grids, or perforated plates similar to those of the catalyst grids **25** in the reactor vessel **11**. The supplementary catalyst promotes the same reaction that occurs in the reaction vessel **11** for any unreacted materials that have been carried over with the product gas drawn from the reaction vessel. Product gas emerging from the supplementary catalyst beds is passed through a condenser **33** and the resulting condensate **34** is directed to the product vessel **12** where it is introduced under the liquid level.

[0018] The liquid level in the product vessel **12** is controlled by a level control **41** which is actuated by a pair of float valves inside the vessel and governs a motor valve **42** on a liquid product outlet line **43** at the base of the vessel. Above the liquid level is a packed bed **44** of conventional tower packings. Examples are Raschig rings, Pall rings, and Intalox saddles; other examples will be readily apparent to those familiar with distillation towers and column packings. The packing material is inert to the reactants and products of the system, or at least substantially so, and serves to entrap liquid droplets that may be present in the gas phase and return the entrapped liquid back to the bulk liquid in the lower portion of the vessel. Unreacted gas **45** is

withdrawn from the head space 46 above the packed bed by a gas pump 47. The pump outlet is passed through a check valve 48 and then directed to the reaction vessel 11 where it enters through the gas distributor 24 positioned between the resistance heater 23 and the catalyst grids 25.

5 [0019] Alternatives to the units described above and shown in the Figure will be readily apparent to the skilled chemical engineer. For example, any known type of condenser can be used to condense the vaporized product from the reaction vessel. Examples of types of condensers are shell-and-tube condensers and plate-and-frame condensers, and among the shell-and-tube condensers are horizontal tube condensers and vertical tube condensers. Either co-
10 current or counter-current condensers can be used, and the condensers can be air-cooled, water-cooled, or cooled by organic coolant media such as automotive anti-freeze (for example, 50% pre-diluted ethylene glycol) and other glycol-based coolants. Alternatives to the resistance heater are heating jackets, heating coils using steam or other heat-transfer fluids, and radiation heaters. Heating of the reaction vessel can also be achieved, either in part or in whole, by
15 recirculation of heat transfer fluid between the coolant side of the condenser and the reaction vessel. The gas distributors for the inlet feed and the recycle gas can be any of a variety of types known in the art. Examples are perforated plates, cap-type distributors, and pipe distributors. The liquid level controls can likewise be any of a variety of mechanisms known in the art. Examples are float-actuated devices, devices measuring hydrostatic head, electrically actuated
20 devices such as those differentiating liquid from gas by electrical conductivity or dielectric constant, thermally actuated devices such as those differentiating by thermal conductivity, and sonic devices based on sonic propagation characteristics.

EXAMPLE 1

[0020] This example illustrates the use of the present invention in a processing system in
25 which the biogas is hydrogen and the reaction medium is mineral oil.

[0021] A catalyst material was prepared by placing the following between two pads of steel wool: aluminum wire, cobalt wire (an alloy containing approximately 50% cobalt, 10% nickel, 20% chromium, 15% tungsten, 1.5% manganese, and 2.5% iron), nickel wire, tungsten wire, and cast iron granules. The material was placed in a reaction vessel over a perforated aluminum

plate, and the vessel was charged with heavy mineral oil, submerging the catalyst material. The vessel contents were then heated to approximately 320-370°F (approximately 160-190°C), and hydrogen gas was bubbled through the vessel at a continuous rate of 60-80 cubic feet per hour (measured at ambient temperature of approximately 25°C), while the pressure in the reactor was maintained at or below 2 psig (approximately 115 KPa). The reaction was continued for five hours, after which time the reaction medium had reduced in volume from 3 parts by volume to 2 parts by volume, and had produced 2.5 parts by volume of condensed product. Values of the kinematic viscosity (taken at 50°C using the protocol of ASTM D 445), flashpoint (by the Pensky-Martens closed-cup method using the protocol of ASTM D 93a), hydrocarbon composition (using the Robinson Modified Method of ASTM D 3239-2425), lubricity (using the high-frequency reciprocating rig method at 60°C with the protocol of ASTM D 6049), vapor pressure (using the dry vapor pressure equivalent method with the protocol of ASTM D 5191), and gross heat of combustion (measured according to the protocol of ASTM D 240) were taken on the reaction medium at the start of the test (mineral oil) and at one and five hours after the start of the test, and on the condensed gaseous product at one and five hours after the start of the test. The results are listed in Table I below.

TABLE I: Test Results for Hydrogen and Mineral Oil

	-----Reaction Medium-----			---Condensed Product---	
	Start of <u>Test</u>	<u>at 1 hour</u>	<u>at 5 hours</u>	<u>at 1 hour</u>	<u>at 5 hours</u>
Kinematic Viscosity (centistokes)	4.524	15.27	4.506	4.499	4.512
Flashpoint (°C)	126.5	151.5	168	74	132
Hydrocarbon Composition (% by weight):	25.01	29.97	34.46	22.24	21.7
Total Paraffins	60.59	59.63	59.74	59.86	63.7
Naphthenes	14.4	10.4	5.8	17.9	14.6
Aromatics					
Lubricity (mm)	0.15	0.24	0.16	0.33	0.3
Vapor Pressure (psi)	0.25	0.25	0.25	1.06	0.48
Gross Heat of Combustion (BTU/lb)	19,572	19,577	19,536	19,505	19,693

[0022] The product was fed to a VAL6 Infrared Oil Heater (Shizuoka Seiki Co., Ltd., Japan) where it burned readily in air. An attempt to use the liquid reaction medium at the start of the test (mineral oil) in the same oil heater was made, and the result was negative, *i.e.*, the medium would not burn.

EXAMPLE 2

[0023] This example illustrates the use of the present invention in a processing system in which the biogas is methane and the reaction medium is mineral oil. Except for the substitution of methane for hydrogen, the test was conducted in the same manner as that of Example 1, using the same materials and operating conditions. The results, measured as in Example 1, are listed in Table II below.

TABLE II: Test Results for Methane and Mineral Oil

	-----Reaction Medium-----			---Condensed Product---	
	Start of <u>Test</u>	<u>at 1 hour</u>	<u>at 5 hours</u>	<u>at 1 hour</u>	<u>at 5 hours</u>
Kinematic Viscosity (centistokes)	4.524	15.11	26.79	4.201	5.967
Flashpoint (°C)	126.5	157	172.5	115	253.5
Hydrocarbon Composition (% by weight):	25.01	31.12	36.6	18.87	23.13
Total Paraffins	60.59	59.08	63	64.83	63.57
Naphthenes	14.4	9.8	0.4	16.3	13.3
Aromatics					
Lubricity (mm)	0.15	0.23	0.19	0.34	0.16
Vapor Pressure (psi)	0.25	0.25	0.25	0.25	0.25

[0024] The product was fed to a VAL6 Infrared Oil Heater (Shizuoka Seiki Co., Ltd., Japan) where it burned readily in air. As in Example 1, the liquid reaction medium at the start of the test (mineral oil) would not burn in the same oil heater.

5

EXAMPLE 3

[0025] This example illustrates the use of the present invention in a processing system in which the biogas is 50% hydrogen and 50% carbon monoxide (by volume) and the reaction medium is mineral oil. Except for the substitution of the hydrogen/carbon monoxide mixture, the test was conducted in the same manner as that of Example 1, using the same materials and operating conditions. The results, measured as in Example 1, are listed in Table III below.

10

TABLE III: Test Results for Hydrogen/Carbon Monoxide and Mineral Oil

	-----Reaction Medium-----			---Condensed Product---	
	Start of <u>Test</u>	<u>at 1 hour</u>	<u>at 5 hours</u>	<u>at 1 hour</u>	<u>at 5 hours</u>
Kinematic Viscosity (centistokes)	4.524	16.84	57.37	4.274	5.797
Flashpoint (°C)	126.5	327.5	0	141	126.5
Hydrocarbon Composition (% by weight):	25.01	25.51	32.01	17.95	21.63
Total Paraffins	60.59	63.49	67.89	65.35	63.87
Naphthenes	14.4	11	0.1	16.7	14.5
Aromatics					
Lubricity (mm)	0.15	0.18	0.17	0.24	0.14
Vapor Pressure (psi)	0.25	0.25	0.25	0.25	0.25

[0026] The product was fed to a VAL6 Infrared Oil Heater (Shizuoka Seiki Co., Ltd., Japan) where it burned readily in air. As in Examples 1 and 2, the liquid reaction medium at the start of the test (mineral oil) would not burn in the same oil heater.

5

EXAMPLE 4

[0027] This example illustrates the use of the present invention in a processing system in which the feed biogas was methane and the liquid petroleum fraction used in the reaction vessel was diesel fuel. The equipment was a pilot version of the plant set forth in the Figure and described above, with a catalyst bed of aluminum wire, cobalt wire (an alloy containing
10 approximately 50% cobalt, 10% nickel, 20% chromium, 15% tungsten, 1.5% manganese, and 2.5% iron), nickel wire, tungsten wire, and cast iron granules. The reaction vessel was 19 inches (0.5 meter) in diameter and initially charged with ten gallons (39 liters) of diesel fuel. The diesel fuel was maintained at a temperature of 240-250°F (116-121°C) and a pressure of 3 psig (122 kPa) as the methane was bubbled through the reactor. After startup, the reactor was run for ten
15 hours, then continued for another 2.5 hours during which time product was collected for analysis.

The volume of product collected was 5.6 liters, and upon completion of the collection, the volume of liquid reaction medium remained at 8-10 gallons (30-39 liters). The product was analyzed by standard ASTM protocols and the results are listed in Table IV.

TABLE IV: Product Test Results

	<u>Protocol</u>	<u>Result</u>	
Flash Point	ASTM D 93	202°F (94°C)	
API Gravity at 60°F (15.6°C)	ASTM D 287	34.8°	
Distillation at 760 mm Hg (1 atm)	ASTM D 86	<u>Percent Recovered:</u>	
		<u>Initial b.p.</u>	423°F (217°C)
		5	452.5°F (234°C)
		10	464.7°F (240°C)
		20	475.5°F (246°C)
		30	485.4°F (252°C)
		40	495.1°F (257°C)
		50	505.2°F (263°C)
		60	516.0°F (269°C)
		70	527.5°F (275°C)
		80	541.6°F (283°C)
		90	560.8°F (294°C)
		95	580.3°F (305°C)
		End	597.9°F (314°C)
Recovery	98.1%		
Residue	1.0%		
Loss	0.9%		
Pressure	765 mm Hg		
Estimated hydrogen content	ASTM D 3343	13.38 weight %	
Particulate Matter	ASTM D 2276	2-0.8µm filters	8.5 mg/gal
		Volume	0.26 gal
		Vacuum	28.3 in. Hg
		Time	10 min
Total Aromatics	ASTM D 1319	18.0 volume %	
Sediment and Water	ASTM D 2709	0 volume %	
Ash	ASTM D 482	0.002 weight %	

Copper Corrosion (3 hours at 122°F, 50°C)	ASTM D 130	1a
Ramsbottom Carbon Residue, 10% Bottoms	ASTM D 524	0.07 weight %
Ramsbottom Carbon Residue	ASTM D 524	0 weight %
Lead	ASTM D 3605	<0.1 ppm
Vanadium	ASTM D 3605	<0.1 ppm
Calcium	ASTM D 3605	<0.1 ppm
Sodium, Potassium, Lithium	ASTM D 3605	<0.1 ppm
Demulsification	ASTM D 1401	5 minutes
Sulfur by X-ray	ASTM D 2622	0.0005 weight %
Cetane Number	ASTM D 613	46.4
Gross Heat of Combustion	ASTM D 240	19,547 BTU/lb, 138,490 BTU/gal

[0028] The product was fed to a VAL6 Infrared Oil Heater (Shizuoka Seiki Co., Ltd., Japan) where it burned readily in air, emitting neither odor nor smoke.

EXAMPLE 5

[0029] This example illustrates the use of the present invention in a processing system in which the feed biogas was natural gas and the liquid petroleum fraction used in the reaction vessel was kerosene. Using equipment of a similar design and layout as that of Example 4 and a catalyst of the same composition, liquid product was formed. The product was tested in both a diesel engine and a gasoline engine, and both engines started cold and ran effectively on the product.

10 [0030] In the claims appended hereto, the term “a” or “an” is intended to mean “one or more.” The term “comprise” and variations thereof such as “comprises” and “comprising,” when preceding the recitation of a step or an element, are intended to mean that the addition of further steps or elements is optional and not excluded. All patents, patent applications, and other

published reference materials cited in this specification are hereby incorporated herein by reference in their entirety. Any discrepancy between any reference material cited herein and an explicit teaching of this specification is intended to be resolved in favor of the teaching in this specification. This includes any discrepancy between an art-understood definition of a word or
5 phrase and a definition explicitly provided in this specification of the same word or phrase.

WHAT IS CLAIMED IS:

- 1 1. A process for producing liquid fuel from a biogas, said method
2 comprising:
3 (a) passing said biogas through a liquid petroleum fraction at a temperature of
4 about 80°C or above but below boiling, while contacting said biogas and said liquid
5 petroleum fraction with a transition metal to produce a gaseous effluent; and
6 (b) condensing said effluent to liquid form.
- 1 2. The process of claim 1 wherein said transition metal is a metal with an
2 atomic number from 23 to 79.
- 1 3. The process of claim 1 wherein said transition metal is a metal with an
2 atomic number from 24 to 74.
- 1 4. The process of claim 1 wherein step (a) is performed while contacting said
2 biogas and said liquid petroleum fraction with a plurality of transition metals in metallic form.
- 1 5. The process of claim 4 wherein said transition metals comprise cobalt,
2 nickel, and tungsten.
- 1 6. The process of claim 4 wherein said transition metals comprise cobalt,
2 nickel, tungsten, and iron.
- 1 7. The process of claim 1 wherein said liquid petroleum fraction is a member
2 selected from the group consisting of mineral oil, diesel oil, naphtha, kerosene, gas oil, and
3 gasoline.
- 1 8. The process of claim 1 wherein step (a) is performed at a temperature of
2 from about 100°C to about 250°C.
- 1 9. The process of claim 1 wherein step (a) is performed at a pressure of from
2 about 1 atmosphere to about 2 atmospheres.

1 **10.** The process of claim 1 wherein said biogas is a member selected from the
2 group consisting of hydrogen, carbon monoxide, methane, and mixtures thereof.

1 **11.** The process of claim 1 wherein said biogas is natural gas.

1 **12.** The process of claim 1 wherein:

2 step (a) comprises feeding biogas to a reaction vessel partially filled with said
3 liquid petroleum fraction to a first externally controlled liquid level to cause said biogas
4 to bubble through said liquid petroleum fraction and through a metallic grid of said
5 transition metal immersed in said liquid; and

6 step (b) comprises performing the following steps continuously and
7 simultaneously with step (a):

8 (i) drawing said effluent from a head space in said reaction vessel above
9 said liquid level through a condenser to convert said gaseous reaction product
10 mixture to liquid condensate and uncondensed gas;

11 (ii) passing said liquid condensate and uncondensed gas into a product
12 vessel having a second externally controlled liquid level, to separate said liquid
13 condensate from said uncondensed gas; and

14 (iii) drawing said liquid condensate so separated from said product vessel,
15 as said liquid fuel, while recycling said uncondensed gas from said product vessel
16 to said reaction vessel by directing said uncondensed gas below said first liquid
17 level and through said first metallic grid.

1 **13.** The process of claim 12 wherein said metallic grid in said reaction vessel
2 is defined as a first metallic grid, said process further comprising passing said gaseous reaction
3 product mixture through a second metallic grid of at least one transition metal prior to said
4 condenser.

1 **14.** The process of claim 13 wherein said second metallic grid is external to
2 said reaction vessel and said product vessel.

1 **15.** The process of claim **12** further comprising passing said uncondensed gas
2 through a fixed bed of inert packing material to recover entrained liquid therein prior to recycling
3 said uncondensed gas to said reaction vessel.

1 **16.** The process of claim **13** wherein said at least one catalytic transition metal
2 constituting said first metallic grid and said at least one catalytic transition metal constituting
3 said second metallic grid are both pluralities of metals comprising cobalt, nickel, and tungsten.

1 **17.** The process of claim **1** wherein:

2 said a reaction vessel is equipped with a first liquid level control means to define
3 minimum and maximum liquid levels, heating means for heating liquid, an inlet gas
4 distributor, a metallic grid of said transition metal, and a vaporized product outlet port,
5 said inlet gas distributor and said first metallic grid positioned below said minimum
6 liquid level, and said vaporized product outlet port positioned above said maximum
7 liquid level;

8 said condenser is arranged to receive said vaporized product emerging from said
9 vaporized product outlet port; and

10 said product vessel is equipped with a second liquid level control means to define
11 minimum and maximum liquid levels.

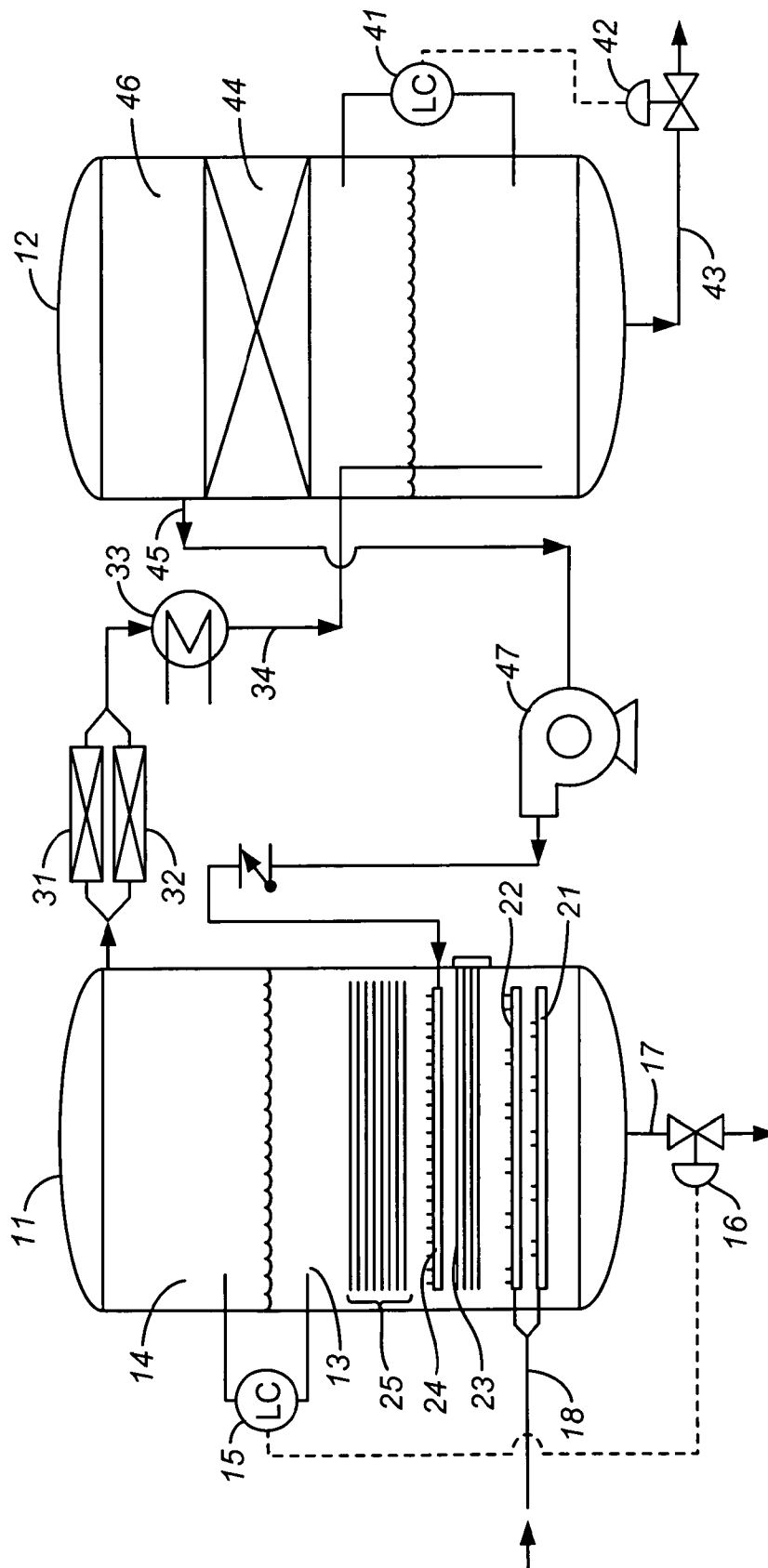


FIGURE 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 09/36054

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01D 46/00 (2009.01)

USPC - 95/273; 55/467.1

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8) - B01D 46/00 (2009.01)

USPC - 95/273; 55/467.1

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

IPC(8) - B01D 19/00, 41/00, 45/00, 47/00, 49/00, 50/00, 51/00, 53/00, 57/00, 59/00 (2009.01)

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

PubWest (PGPB,USPT,USOC,EPAB,JPAB); Google

Google Search Terms Used:

liquefying biogas, torrefaction, Fischer-Tropsch low temperature, low pressure fischer tropsch, fischer tropsch fixed bed condenser

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/0142481 A1 (STEYNBERG et al.) 21 June 2007 (21.06.2007), para [0042-0060]	1-3, 8, 10 and 11
Y		4-7, 9 and 12-17
Y	US 2006/0054865 A1 (SMITH et al.) 16 March 2006 (16.03.2006), para [0029]	4-6 and 16
Y	US 6,068,760 A (BENHAM et al.) 30 May 2000 (30.05.2000), col 3, ln 1-3	7
Y	US 5,728,918 A (NAY et al.) 17 March 1998 (17.03.1998), col 3, ln 29-35	9
Y	US 2002/0035036 A1 (FIGUEROA et al.) 21 March 2002 (21.03.2002), para [0051]	12-14, 16 and 17
Y	US 2006/0287560 A1 (XIE) 21 December 2006 (21.12.2006), para [0023]	15
Y	US 2005/0027020 A1 (STEYNGERG) 03 February 2005 (03.02.2005), (para [0044-0048])	17

Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

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Date of mailing of the international search report

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Name and mailing address of the ISA/US
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450
Facsimile No. 571-273-3201

Authorized officer:
Lee W. Young

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774