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Operation of a steam hydro-gasifier in a fluidized bed reactor

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Norbeck et al. (43) **Pub. Date: Jan. 24, 2008**(54) **OPERATION OF A STEAM  
HYDRO-GASIFIER IN A FLUIDIZED BED  
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**C07C 27/06** (2006.01)(52) **U.S. Cl.** ..... **518/702**(57) **ABSTRACT**

Carbonaceous material, which can comprise municipal waste, biomass, wood, coal, or a natural or synthetic polymer, is converted to a stream of methane and carbon monoxide rich gas by heating the carbonaceous material in a fluidized bed reactor using hydrogen, as fluidizing medium, and using steam, under reducing conditions at a temperature and pressure sufficient to generate a stream of methane and carbon monoxide rich gas but at a temperature low enough and/or at a pressure high enough to enable the carbonaceous material to be fluidized by the hydrogen. In particular embodiments, the fluidizing mixture can be a combination of hydrogen and steam. The stream of methane and carbon monoxide rich gas can be subjected to steam methane reforming under conditions whereby synthesis gas comprising hydrogen and carbon monoxide is generated. Synthesis gas generated by the steam methane reforming is fed into a Fischer-Tropsch reactor under conditions whereby a liquid fuel is produced. Excess hydrogen from the steam methane reformer can be fed back to the fluidized bed reactor. Exothermic heat from the Fischer-Tropsch reaction can be transferred to the hydro-gasification reactor.

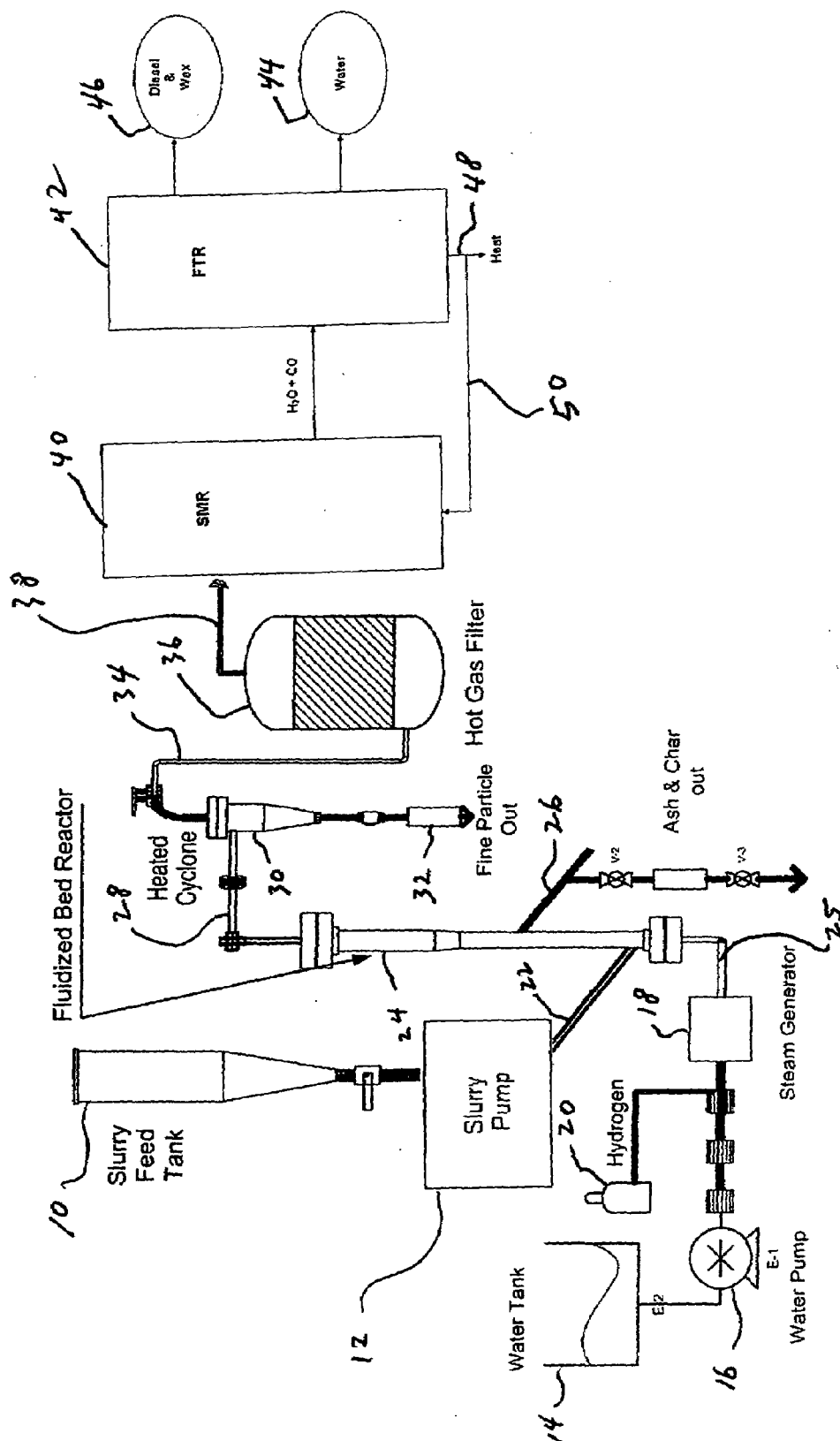


Fig. 1

## OPERATION OF A STEAM HYDRO-GASIFIER IN A FLUIDIZED BED REACTOR

### FIELD OF THE INVENTION

**[0001]** The field of the invention is the synthesis of transportation fuel from carbonaceous feed stocks.

### BACKGROUND OF THE INVENTION

**[0002]** There is a need to identify new sources of chemical energy and methods for its conversion into alternative transportation fuels, driven by many concerns including environmental, health, safety issues, and the inevitable future scarcity of petroleum-based fuel supplies. The number of internal combustion engine fueled vehicles worldwide continues to grow, particularly in the midrange of developing countries. The worldwide vehicle population outside the U.S., which mainly uses diesel fuel, is growing faster than inside the U.S. This situation may change as more fuel-efficient vehicles, using hybrid and/or diesel engine technologies, are introduced to reduce both fuel consumption and overall emissions. Since the resources for the production of petroleum-based fuels are being depleted, dependency on petroleum will become a major problem unless non-petroleum alternative fuels, in particular clean-burning synthetic diesel fuels, are developed. Moreover, normal combustion of petroleum-based fuels in conventional engines can cause serious environmental pollution unless strict methods of exhaust emission control are used. A clean burning synthetic diesel fuel can help reduce the emissions from diesel engines.

**[0003]** The production of clean-burning transportation fuels requires either the reformulation of existing petroleum-based fuels or the discovery of new methods for power production or fuel synthesis from unused materials. There are many sources available, derived from either renewable organic or waste carbonaceous materials. Utilizing carbonaceous waste to produce synthetic fuels is an economically viable method since the input feed stock is already considered of little value, discarded as waste, and disposal is often polluting.

**[0004]** Liquid transportation fuels have inherent advantages over gaseous fuels, having higher energy densities than gaseous fuels at the same pressure and temperature. Liquid fuels can be stored at atmospheric or low pressures whereas to achieve liquid fuel energy densities, a gaseous fuel would have to be stored in a tank on a vehicle at high pressures that can be a safety concern in the case of leaks or sudden rupture. The distribution of liquid fuels is much easier than gaseous fuels, using simple pumps and pipelines. The liquid fueling infrastructure of the existing transportation sector ensures easy integration into the existing market of any production of clean-burning synthetic liquid transportation fuels.

**[0005]** The availability of clean-burning liquid transportation fuels is a national priority. Producing synthesis gas (which is a mixture of hydrogen and carbon monoxide) cleanly and efficiently from carbonaceous sources, that can be subjected to a Fischer-Tropsch process to produce clean and valuable synthetic gasoline and diesel fuels, will benefit both the transportation sector and the health of society. Such a process allows for the application of current state-of-art engine exhaust after-treatment methods for NO<sub>x</sub> reduction,

removal of toxic particulates present in diesel engine exhaust, and the reduction of normal combustion product pollutants, currently accomplished by catalysts that are poisoned quickly by any sulfur present, as is the case in ordinary stocks of petroleum derived diesel fuel, reducing the catalyst efficiency. Typically, Fischer-Tropsch liquid fuels, produced from biomass derived synthesis gas, are sulfur-free, aromatic free, and in the case of synthetic diesel fuel have an ultrahigh cetane value.

**[0006]** Biomass material is the most commonly processed carbonaceous waste feed stock used to produce renewable fuels. Waste plastic, rubber, manure, crop residues, forestry, tree and grass cuttings and biosolids from waste water (sewage) treatment are also candidate feed stocks for conversion processes. Biomass feed stocks can be converted to produce electricity, heat, valuable chemicals or fuels. California tops the nation in the use and development of several biomass utilization technologies. Each year in California, more than 45 million tons of municipal solid waste is discarded for treatment by waste management facilities. Approximately half this waste ends up in landfills. For example, in just the Riverside County, California area, it is estimated that about 4000 tons of waste wood are disposed of per day. According to other estimates, over 100,000 tons of biomass per day are dumped into landfills in the Riverside County collection area. This municipal waste comprises about 30% waste paper or cardboard, 40% organic (green and food) waste, and 30% combinations of wood, paper, plastic and metal waste. The carbonaceous components of this waste material have chemical energy that could be used to reduce the need for other energy sources if it can be converted into a clean-burning fuel. These waste sources of carbonaceous material are not the only sources available. While many existing carbonaceous waste materials, such as paper, can be sorted, reused and recycled, for other materials, the waste producer would not need to pay a tipping fee, if the waste were to be delivered directly to a conversion facility. A tipping fee, presently at \$30-\$35 per ton, is usually charged by the waste management agency to offset disposal costs. Consequently not only can disposal costs be reduced by transporting the waste to a waste-to-synthetic fuels processing plant, but additional waste would be made available because of the lowered cost of disposal.

**[0007]** The burning of wood in a wood stove is a simple example of using biomass to produce heat energy. Unfortunately, open burning of biomass waste to obtain energy and heat is not a clean and efficient method to utilize the calorific value. Today, many new ways of utilizing carbonaceous waste are being discovered. For example, one way is to produce synthetic liquid transportation fuels, and another way is to produce energetic gas for conversion into electricity.

**[0008]** Using fuels from renewable biomass sources can actually decrease the net accumulation of greenhouse gases, such as carbon dioxide, while providing clean, efficient energy for transportation. One of the principal benefits of co-production of synthetic liquid fuels from biomass sources is that it can provide a storable transportation fuel while reducing the effects of greenhouse gases contributing to global warming. In the future, these co-production processes could provide clean-burning fuels for a renewable fuel economy that could be sustained continuously.

**[0009]** A number of processes exist to convert coal, biomass, and other carbonaceous materials to clean-burning

transportation fuels, but they tend to be too expensive to compete on the market with petroleum-based fuels, or they produce volatile fuels, such as methanol and ethanol that have vapor pressure values too high for use in high pollution areas, such as the Southern California air-basin, without legislative exemption from clean air regulations. An example of the latter process is the Hynol Methanol Process, which uses hydro-gasification and steam reformer reactors to synthesize methanol using a co-feed of solid carbonaceous materials and natural gas, and which has a demonstrated carbon conversion efficiency of >85% in bench-scale demonstrations.

**[0010]** Of particular interest to the present invention are processes developed more recently in which a slurry of carbonaceous material is fed into a hydro-gasifier reactor. One such process was developed in our laboratories to produce synthesis gas in which a slurry of particles of carbonaceous material in water, and hydrogen from an internal source, are fed into a hydro-gasification reactor under conditions to generate rich producer gas. This is fed along with steam into a steam pyrolytic reformer under conditions to generate synthesis gas. This process is described in detail in Norbeck et al. U.S. patent application Ser. No. 10/503,435 (published as US 2005/0256212), entitled: "Production Of Synthetic Transportation Fuels From Carbonaceous Material Using Self-Sustained Hydro-Gasification."

**[0011]** In a further version of the process, using a steam hydro-gasification reactor (SHR) the carbonaceous material is heated simultaneously in the presence of both hydrogen and steam to undergo steam pyrolysis and hydro-gasification in a single step. This process is described in detail in Norbeck et al. U.S. patent application Ser. No. 10/911,348 (published as US 2005/0032920), entitled: "Steam Pyrolysis As A Process to Enhance The Hydro-Gasification of Carbonaceous Material." The disclosures of U.S. patent application Ser. Nos. 10/503,435 and 10/911,348 are incorporated herein by reference.

**[0012]** Fluidized bed reactors are well known and used in a variety of industrial manufacturing processes, for example in the petroleum industry to manufacture fuels as well as in petrochemical applications including coal gasification, fertilizers from coal, and industrial and municipal waste treatment. Because the operation of the fluidized bed reactor is generally restricted to temperatures below the softening point of the material being processed and slugging of materials such as ash will disturb the fluidization of the bed, fluidized bed reactors have had little if any use in the processing of many of the types of carbonaceous materials used as feed in hydro-gasification reactions. Moreover, tar formation is a typical problem of low temperature fluidized bed gasifiers with conventional technology. These problems can be amplified when scaling up. For example, attempts to scale up the Fischer-Tropsch synthesis failed as described by Werther et al. in "Modeling of Fluidized Bed Reactors," International Journal of Chemical Reactor Engineering, Vol. 1:P1, 2003.

#### BRIEF SUMMARY OF THE INVENTION

**[0013]** Notwithstanding the above drawbacks, the present inventors realized that feedstocks used in hydro-gasification reactions, such as coal and biomass, can be sufficiently reactive to operate at the lower temperatures of fluidized bed processes. This invention provides an improved, economical

alternative method of conducting hydro-gasification, by operating the hydro-gasification in a fluidized bed reactor. Use of a fluidized bed to conduct hydro-gasification provides extremely good mixing between feed and reacting gases, which promotes both heat and mass transfer. This ensures an even distribution of material in the bed, resulting in a high conversion rate compared to other types of gasification reactors.

**[0014]** Moreover, we have found that the steam hydro-gasification reaction (SHR), such as described in the above-referred-to U.S. patent application Ser. No. 10/911,348, is particularly well suited for being conducted in a fluidized bed reactor. Because SHR usually is operated under the ash slugging temperature, the hydrogen feed of the SHR, optionally combined with the steam, can be used as the fluidized medium. The reducing environment of hydro-gasification suppresses tar formation, which avoids the problems described above.

**[0015]** In a particular implementation of the invention, the output of the fluidized bed reactor is used as feedstock for a steam methane reformer (SMR), which is a reactor that is widely used to produce synthesis gas for the production of liquid fuels and chemicals, for example in a Fischer-Tropsch reactor (FTR).

**[0016]** More particularly in the present invention, carbonaceous material, which can comprise municipal waste, biomass, wood, coal, or a natural or synthetic polymer, is converted to a stream of methane and carbon monoxide rich gas by heating the carbonaceous material in a fluidized bed reactor using steam and/or hydrogen, preferably both, as fluidizing medium at a temperature and pressure sufficient to generate a stream of methane and carbon monoxide rich gas but at a temperature low enough and/or at a pressure high enough to enable the carbonaceous material to be fluidized by the hydrogen or by a mixture of hydrogen and steam. Preferably, the temperature is about 790° C. to about 850° C. at a pressure of about 132 psi to 560 psi. Impurities are removed from the stream of methane and carbon monoxide rich gas, preferably at substantially the temperature at which the carbonaceous material is heated, which can if desired use the same pressure.

**[0017]** In a preferred method, the stream of methane and carbon monoxide rich gas is subjected to steam methane reforming under conditions whereby synthesis gas comprising hydrogen and carbon monoxide is generated. In a further preferred method, synthesis gas generated by the steam methane reforming is fed into a Fischer-Tropsch reactor under conditions whereby a liquid fuel is produced. Exothermic heat from the Fischer-Tropsch reaction can be transferred to the hydro-gasification reaction and/or steam methane reforming reaction.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0018]** For a more complete understanding of the present invention, reference is now made to the following description taken in conjunction with the accompanying drawing, in which:

**[0019]** FIG. 1 is a schematic flow diagram of a specific implementation in which a steam hydro-gasification reaction is conducted in a fluid bed reactor.

# DETAILED DESCRIPTION OF THE INVENTION

[0020] Referring to FIG. 1, Apparatus is shown for a process for converting carbonaceous material such as municipal waste, biomass, wood, coal, or a natural or synthetic polymer to a methane and carbon monoxide rich gas. The carbonaceous material in the form of a slurry is loaded into a slurry feed tank 10 and gravity fed to a slurry pump 12. In this embodiment, water from a water tank 14 is fed by a water pump 16 to a steam generator 18. Simultaneously, hydrogen is fed to the steam generator 18, which can be from a tank 20 of hydrogen, from an internal source such as the output from a downstream steam methane reformer (as will be described below), or from both. The output of the slurry pump 12 is fed through line 22 to the bottom of a fluidized bed reactor 24 while the output from the steam generator 18 is fed through line 25 to the fluidized bed reactor 24 at a point below the slurry of carbonaceous material.

[0021] In another embodiment, the hydrogen is fed directly to the fluidized bed reactor 24 at a point below the slurry of carbonaceous material while the feed from the steam generator is introduced at a point above the input of the slurry of carbonaceous material, i.e., downstream of the point of introduction of the carbonaceous material.

[0022] The fluidized bed reactor 18 operates as a steam hydro-gasification reactor (SHR) at a temperature of about 790° C. to about 850° C. and pressure about 132 psi to 560 psi to generate a stream of methane and carbon monoxide rich gas, which can also be called a producer gas. The chemical reactions taking place in this process are described in detail in Norbeck et al. U.S. patent application Ser. No. 10/911,348 (published as US 2005/0032920), entitled: "Steam Pyrolysis As A Process to Enhance The Hydro-Gasification of Carbonaceous Material." The disclosure of U.S. patent application Ser. No. 10/911,348 is incorporated herein by reference.

[0023] The ash slagging temperature in the fluidized bed reactor 24 is sufficiently low and the pressure sufficiently high that a fluidized bed reaction can be use. The reducing environment of fluidized bed reactor 24 also suppresses tar formation.

[0024] Ash and char, as well as hydrogen sulfide and other inorganic components from the fluidized bed reactor 18 are disposed of through line 26 and its output is fed through line 28 into a heated cyclone 30 which separates out fine particles at 32. The output from the heated cyclone 30 is fed through line 34 to a hot gas filter 36, then through line 38 to a steam methane reactor 40.

[0025] At the steam methane reformer 40, synthesis gas is generated comprising hydrogen and carbon monoxide at a  $H_2:CO$  mole ratio range of about 3 to 1. The hydrogen/carbon monoxide output of the steam methane reformer 40 can be used for a variety of purposes, one of which is as feed to a Fischer-Tropsch reactor 42 from which pure water 44 and diesel fuel and/or wax 46. Exothermic heat 48 from the Fischer-Tropsch reactor 42 can be transferred to the steam methane reformer 40 as shown by line 50.

[0026] The required  $H_2:CO$  mole ratio of a Fischer-Tropsch reactor with a cobalt based catalyst is 2:1. Accordingly,

there is an excess of hydrogen from the steam methane reformer 40, which can be separated and fed into the fluidized bed reactor 24 (by lines not shown) to make a self-sustainable process, i.e., without requiring an external hydrogen feed.

[0027] Although the present invention and its advantages have been described in detail, it should be understood that various changes, substitutions and alterations can be made herein without departing from the spirit and scope of the invention as defined by the appended claims. Moreover, the scope of the present application is not intended to be limited to the particular embodiments of the process and apparatus described in the specification. As one of ordinary skill in the art will readily appreciate from the disclosure of the present invention, processes and apparatuses, presently existing or later to be developed that perform substantially the same function or achieve substantially the same result as the corresponding embodiments described herein may be utilized according to the present invention. Accordingly, the appended claims are intended to include such processes and use of such apparatuses within their scope.

1. A process for converting carbonaceous material to a stream of methane and carbon monoxide rich gas, comprising:

heating carbonaceous material in a fluidized bed reactor using hydrogen as fluidizing medium, and using steam, at a temperature and pressure sufficient to generate a stream of methane and carbon monoxide rich gas but at a temperature low enough and/or at a pressure high enough to enable the carbonaceous material to be fluidized by the steam and/or hydrogen.

2. The process of claim 1 in which a combination of hydrogen and steam is used as the fluidizing medium.

3. The process of claim 1 in which the steam is used introduced downstream from the point of introduction of the carbonaceous material.

4. The process of claim 1 including the step of removing impurities from the stream of methane and carbon monoxide rich gas.

5. The process of claim 4 in which the impurities are removed from the stream of methane and carbon monoxide rich gas at substantially the temperature at which the carbonaceous material is heated.

6. The process of claim 5 in which the impurities are removed from the stream of methane and carbon monoxide rich gas at substantially the pressure of the fluidized bed reactor.

7. The process of claim 1 including the step of subjecting the stream of methane and carbon monoxide rich gas to steam methane reforming under conditions whereby synthesis gas comprising hydrogen and carbon monoxide is generated.

8. The process of claim 7 in which synthesis gas generated by the steam methane reforming is fed into a Fischer-Tropsch reactor under conditions whereby a liquid fuel is produced.

9. The process of claim 1 conducted under reducing conditions.

10. The process of claim 1 wherein the temperature is about 790° C. to about 850° C.

11. The process of claim 10 wherein the pressure is about 132 psi to 560 psi.

**12.** The process of claim **1** wherein the carbonaceous material comprises municipal waste, biomass, wood, coal, or a natural or synthetic polymer.

**13.** A process for converting municipal waste, biomass, wood, coal, or a natural or synthetic polymer to synthesis gas, comprising:

simultaneously heating carbonaceous material under reducing conditions in a fluidized bed reactor using hydrogen as fluidizing medium, and using steam, at a temperature of about 790° C. to about 850° C. and pressure about 132 psi to 560 psi whereby to generate a stream of methane and carbon monoxide rich producer gas;

removing impurities from the producer gas stream substantially at said temperature and pressure;

subjecting the resultant producer gas to steam methane reforming under conditions whereby to generate synthesis gas comprising hydrogen and carbon monoxide at a H<sub>2</sub>:CO mole ratio range of 2:1 to 6; and

feeding synthesis gas generated by the steam methane reforming into a Fischer-Tropsch reactor under conditions whereby a liquid fuel is produced.

**14.** The process of claim **13** comprising transferring exothermic heat from the Fischer-Tropsch reaction to the hydro-gasification reaction and/or steam methane reforming reaction.

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