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Title: A BIOMASS GASIFICATION METHOD AND APPARATUS FOR PRODUCTION OF SYNGAS WITH A RICH HYDROGEN CONTENT

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A BIOMASS GASIFICATION METHOD AND APPARATUS FOR PRODUCTION OF SYNGAS WITH A RICH HYDROGEN CONTENT

BACKGROUND OF THE INVENTION

This invention relates to thermal gasification processes and in particular to biomass gasification processes. Thermal gasification is the process of converting carbonaceous materials, such as coal, petroleum coke, biomass, and/or solid waste etc. into combustible gases. The combustible gases are primarily hydrogen and carbon monoxide mixed with lesser amounts of carbon dioxide, water, methane, higher hydrocarbons, and nitrogen. Air, steam, and oxygen, either alone or in any combination thereof, are often used as gasification agents. Using pure steam as gasification medium is very attractive since the caloric value of produced syngas can be much higher due to no dilution by N₂ and CO₂. The syngas also has higher hydrogen content. Generally, factors that affect the performance of the thermal gasification reactor system include: stoichiometry of reactants, gasification temperature and pressure, heating rate of feedstock, kind of gasifying agents, residence time, feedstock properties, and catalyst or bed additives.

The thermal gasification processes are highly endothermic chemical reactions. The general methods for supplying heat for the gasification include: a) an outside source, e.g. hot char recirculation, and/or sensible heat from a gasification agent, b) reaction heat from oxidization of a part of feedstock (incoming carbonaceous materials), and c) exothermical reaction heat from a non-carbonaceous material such as calcined lime and CO₂.

The application of the technology of partial combustion of incoming carbonaceous materials is widely adopted. By the technology, the non combustible gas, CO₂, is produced and as it is not removed it leads to a diluted syngas, and the LCV (low caloric value, a measure for the burning value of the dry gas mass) of the produced syngas becomes limited. Moreover, the existing CO₂ leads to a small partial pressure of other gas species, which is not favorable for other valuable
gasification reactions, for example, the water-gas shift reaction. Thus, the hydrogen content in the syngas will be affected.

The idea of supplementing most of the energy using sensible heat for the gasification process has recently been considered, and positive results have been shown. For example, the invention of Yoshikawa, Kunio (Sagamihara-shi, JP) and Suzuki, Narumi (Tajimi-shi, JP) of US 2004/0060236, "Apparatus for gasifying solid fuel", teaches an economic small scale gasification system for gasifying solid fuel into pyrolysis gas in which heated steam/air is introduced into a reformer along with the pyrolysed gas producing reformed high temperature crude gas. Here, high temperature steam/air will be obtained mainly by use of a honeycomb regenerative heat exchanger explained in, for example, patent US 6,837,910. The temperature of hot gasifying medium cannot be over 1600K (1323°C). If pure steam is used for the gasification process using the regenerative heat exchanger, the temperature of the steam will be at the level of 700 -1250°C. Thus, the quantities of H₂ and CO produced per unit of steam are very low. This leads to an uneconomic gasification.

Other known systems using high-temperature air/steam/oxygen as high as 1000°C for a biomass/waste gasification process have also been applied (Lucas C., Szewczyk D., Blasiak W., Mochida S., High Temperature Air and Steam Gasification of Densified Biofuels, Biomass and Bioenergy, Volume 27, Issue 6, December 2004, Pages 563-575). A char free hydrogen rich gas, where the process is performed with only steam at a temperature of 1000°C and at a conventional pressure of about 1 atm has been proposed (Ponzio Anna, Yang Weihong., Lucas, C, Blasiak W., Development of a Thermal Homogenous Gasifier System using High Temperature Agent, CLEAN AIR - International Journal on Energy for a Clean Environment, Vol. 7, No. 4., 2007).

Further development of using high-temperature agents for gasification process, i.e. pure steam for gasification, is described in for example US 2003/0233788, of Lewis, Frederick Michael (El Segundo, CA) "Generation of an ultra-superheated steam composition and gasification therewith", where a new method using the sensible heat of the steam is proposed. It is a method for
gasifying carbonaceous materials into fuel gases. It involves the formation of an ultra-superheated steam (USS) composition substantially containing water vapor, carbon dioxide and highly reactive free radicals thereof, at a high temperature 2000°F (1316°C) to about 5000°F (2760°C). The USS flame is contacted with a carbonaceous material for rapid gasification/reforming thereof. In addition, a controlled amount of oxygen for oxidation of fuel for heating the steam has to be used, increasing the operation cost. Additionally, when the pure steam temperature is less than 2075K (1802°C), a surplus of steam is still required to convert all the carbon. Moreover, the carbon conversion rate is also low. All these restrictions may make the process uneconomical, especially for the small scale gasifier system.

It is well known that using pure steam as a gasification medium can increase syngas quality. However, the gasification process using pure steam is extremely endothermic. If all the gasification energy is supplied by the sensible energy carried by the gasification agent, the temperature of gas has to be very high. For example, if we consider the gasification reaction between carbon and steam, the steam temperature is at least 2075K (1802°C) in order to have a theoretical stoichiometric ratio. Thus, at lower temperatures either a long residence time or a larger amount of excess steam is required. This leads to low process efficiency and corresponding high economic costs. For example, when even a modern regenerative heat exchanger is used as in US 6,837,910, assigned to Japan Science and Technology Agency, the temperature of the steam is at the level of 700-1250°C. Considering the wall/pipe/ system heat loss that will be obtained in an embodiment of the technology, larger quantities of excess and not reacted steam have to be used.

It is important to notice, that with a steam temperature increase, the hydrogen concentration in the produced gas is decreased since the water-shift reaction is an exothermic reaction. In this case, a lower ratio of \( \text{H}_2: \text{CO} \) in the generated gas occurs.

Moreover, in order to obtain medium and high LCV of syngas using pure steam as agent, where the carbon conversion ratio of biomass is normally 70-80%,
a reasonable high flow rate of the steam has to be used even though the temperature of the steam is high. Thus, the yields of syngas may be further increased by also applying a high flow rate of the steam.

Described in the herein disclosed invention is a novel process drastically improving the above described gasification technologies. Instead of obtaining the extra heat by partial combustion of incoming carbonaceous materials the herein described invention supplies extra heating using reaction heat from non-carbonaceous materials such as calcined lime and CO₂. This is done in order to increase the hydrogen concentrations in the syngas and the thermal conversion ratio of the feedstock.

In the disclosed invention, the high-temperature air/steam can be obtained using either a modern regenerative heat exchanger (US 6,837,910), or the technical methods described herein.

Using reacting heat from e.g. calcined lime and CO₂ has been tested widely. An example using the heat from the reaction between CaO and CO₂ supplied by oxidation of a part of the solid fuel is published in US 4,191,540. In this case, CaO particles are generally used as the gasifier bed materials to induce an on-site CO₂ capture via

\[ \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \quad \text{exothermic reaction -42.5 kcal} \]

Thus, the syngas has a low CO₂ content and a high caloric value. In a calciner coupled to the gasifier, the formed CaCO₃ was regenerated into CaO and reused through recirculation. Since the above equation is a volume-reducing reaction, high pressure was commonly used. Additionally, reasonable low reaction temperatures are needed to prevent the CaCO₃ calcination, i.e.

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]

Because of these facts the gasification process using Ca-based material is operated generally at 1000-1100 K and >=20atm to produce a high caloric pipeline gas from coal or coal coke. In US Patent No. 4,191,540) a fluidized bed reactor is used. The gasification reaction heat needed is only supported by the carbonate reaction and partial oxidization of solid fuel. High-temperature steam over 1000 K
is not used or taught. The process was further investigated and improved by elevating the pressure up to >30 atm and a relatively low temperature steam (about 873K) integrating the carbon fixation and the gasification process in the so-called Hy-Pr-RING process (US 7,014,834 B2).

A paper by Lin et al., Energy Conversion and Management, 43, (2002), 1283-1290 discusses the above Hy-Pr-RING process where the chemical reactions are integrated into one reactor. The process was first developed on coal, but later on developed to run entirely on water and a carbon fuel. It was shown that low temperatures (below 900°C) at high pressures using steam resulted in 90% hydrogen gas; also on organic waste.

If CaO is added in a sufficient amount in order to absorb all the formed CO₂ the pressure should be at least 220 atm and the temperature not lower than 600°C. As this is not realistic to achieve at a reasonable cost of equipment and operational safety another solution has to be provided. This is stated in US 7,014,834 B2.

From all of the above known prior art, it can be seen that the main gasification reaction heat is supported by the fixation of CO₂ by CaO combined with partial oxidization of solid fuel, i.e. not by using the sensible heat of high temperature steam. Additionally, a relative higher pressure is needed in order to achieve a reasonable CO₂ capture.

In the herein disclosed invention biomass gasification with high temperature steam/air gasification agents and Ca-Based CO₂ sorbents at atmospheric pressure are used and the gasification process temperature is around 1000K. High-temperature steam is not only acting as a gasification agent, but also acting as an energy supplement.

Moreover, gasification invariably results in the formation of three major classes of products: a) a mixture of gases (H₂, CO, CO₂, CH₄ and N₂ and small part of big molecular hydrocarbons), b) tar, and 3) solid residues. The fuel gases have to be cleaned for use in internal combustion engines, gas turbines or other applications requiring high-quality gas. Generally, the tar and solid residues from
the gasifiers available on the market today do not meet acceptable values when operated without gas cleaning.

Typical values to be achieved for use in gas turbines are: particulates < 1 ppm, tar < 5 mg/m³, HCl < 0.5 ppm, S (H₂S+SO₂ etc.) at the level of 1 ppm, Na < 1ppm, K< 1ppm, and other metals < 1 ppm (Bridgewater, A.V., Beenackers A.A.C.M., Sipila, K., Zhenhong, Y., Chuangzhi W. and Li S., An assessment of the possibilities for transfer of European biomass gasification technology to China). For gas engines, maximum allowable concentration of particulates is < 50 mg/m³, and tar < 100 mg/m³. Turbocharged engines make an even higher demand on gas quality and in order to avoid fouling and deposits in the engine, the gas should be to a large degree tar- and dust-free (Bridgewater, A.V. and Evans G.D., An assessment of thermochemical conversion systems for processing biomass and refuse, Energy Technology Support Unit (ETSU) on behalf of the Department of Trade, ETSU B/T1/00207/REP, 1993).

Gas cleaning can be achieved by two basic gas treatment methods: hot gas filtration and wet gas scrubbing. It is obvious that direct treatment of the hot syngas from the gasifier gives the highest process efficiencies.

In order to perform the hot gas cleaning or hot gas conditioning, generally, a catalyst is used for this reforming process. However, in order to avoid poisoning and fouling of a catalyst, high temperature syngas has to been cleaned (tar removal, other elements, mainly S and HCl) and cooled; for example, as in patent US 2004/0060236. In such a type of gasification system, the thermal efficiency of the whole system is low. In order to prevent such a heat loss, the steam reforming process is considered to be employed, in which steam is mixed with the thermal decomposed gas so as to reform the hydrocarbon in the thermal decomposed gas by means of a steam reforming reaction as done in patent US 6,837,910 B1. Another way is to let the thermal decomposed gas pass through a bed packed with CaO-based particles, for example, as by Delgado J., Aznar M.P., and Corella. J., Biomass gasification with steam in fluidized bed: effectiveness of CaO, MgO, and CaO-MgO for hot gas cleaning, Ind Eng. Chem, Res, 1997, 36, 1535-1543.
In the first case, since only high-temperature steam is injected into the reformer in an amount for enough reactant to be present, the sensible heat from this high-temperature steam is not enough to satisfy the energy need for the steam reforming process. Extra heat or air/oxygen has to be injected into the reformer. This consumes syngas. For the second method by Delgado J., Aznar M.P., and Corella. J., Biomass gasification with steam in fluidized bed: effectiveness of CaO, MgO, and CaO-MgO for hot gas cleaning, Ind Eng. Chem, Res, 1997, 36, 1535-1543, CaO-based material is only added in order to work as a catalyst for the oxidation of CO and tar reforming/cracking.

In the disclosed invention, a hot gas clean/conditioning is proposed. The unique method of promoting steam reforming and water-shift reactions through increasing steam partial pressure by injection high-temperature steam to as high as 1000 K, and decreasing CO₂ partial pressure by CO₂ absorption by CaO is neither taught nor disclosed in any of the above discussed prior art.

Thus, the object of the present invention is to provide a thermal gasification method and an apparatus for production of syngas with a medium or high LCV (lower caloric value), rich in hydrogen and with only minor amounts of char, tar, and other particulates.

Another object of the present invention is to provide a thermal gasification process and an apparatus in which a maximal quantity of usable syngas per unit of steam introduced into the gasifier is produced.

Another object of the present invention is to provide a thermal gasification process and an apparatus, in which a maximal quantity of usable syngas rich in hydrogen per unit of CaO introduced into the gasifier is generated.

Another object is to provide a method and an apparatus in which a maximal quantity of hydrogen gas per unit of steam, and/or per unit of calcined lime consumed is produced. The relative importance of these two parameters is optimized with respect to the overall economy.
Another object of the present invention is the use of an apparatus to
generate a high temperature gasification agent (steam/air/oxygen) of a temperature
in the range of 800 to 1600°C for the proposed thermal gasification.

Another object is to provide a method for controlling a thermal gasification
process for gasification at conditions optimal with respect to raw materials
consumption, yield, the ratio of H₂:CO of final product, and cost.

Other objects and advantages of the present invention will become obvious
to the reader and it is intended that these objects and advantages are within the
scope of the present invention.

SUMMARY OF THE INVENTION

The invention herein relates to a method and apparatus for gasifying
carbonaceous materials. More particularly, the invention relates to a method and
apparatus for generating a high quality syngas rich in hydrogen by gasifying solid
fuel or solid carbonaceous materials, such as biomass by a thermal conversion
process.

The disclosed invention provides a gasification process whereby the
gasification energy is supplied by the sensible heat carried by the high temperature
agent (even pure steam) as high as 1000 K combined with the heat released by the
chemical reaction between calcined lime and carbon dioxide.

It is found that a gasification system comprising a high temperature
steam/air/oxygen gasifier including adding CO₂ directly into the gasifier, or
including a syngas reformer, together with a CO₂ recovery system, can form an
efficient gasification system for gasification of solid fuel such as biomass. The
system comprises a gasification step using high temperature steam in excess to
supply the required extra heat in a first reactor for production of syngas, and either
adding CaO together or separately from the water/steam to the gasifier in a first
embodiment, or to a refining process of the produced syngas for capturing the
formed carbon dioxide in a second reactor in a second embodiment, followed by separation of the hydrogen gas from particulates in a separator, and recovering of the absorbent by a heating step. These processes turned out to have a satisfactory efficiency regarding moles of steam used per moles of hydrogen produced, and a medium and high LCV value for the hydrogen gas.

The required heat of the process according to the present invention is provided by the sensible heat of the hot steam and the heat of the reaction between CaO and CO₂. In the present invention CaO is provided at normal grade.

The process according to the present invention does not require high pressures. In the first embodiment of the invention, the pressure of a first reactor, a gasifier, is working at 1 atm and in the temperature range from 600 to 900°C.

In the second embodiment of the invention the pressure of a first reactor, a gasifier is working at 1 atm and in the temperature range from 800 to 1600°C. The syngas from the gasifier enters a second refining reactor. The pressure of this second reactor is 1 atm and the temperature from 600 to 900°C.

Preferably, a ratio of steam to carbon source is in the range of 1.6:1 or higher is used.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG.1 is a generalized flow diagram illustrating a preferred arrangement of the first type of embodiment of a solid fuel gasifying apparatus according to the invention. It shows a novel gasification process for biomass and solid waste.

FIG.2 is a general side view of a heat exchanger to heat low temperature gases (steam/air/oxygen) up to 1000°C using a ball type regenerator which is representative of the heat exchanger useful in the practice of the invention.

FIG.3 is a general side view of another type of heat exchanger to heat low temperature gases (steam/air/oxygen) up to 1300°C using a rotary honeycomb type regenerator, which is representatives of the heat exchanger useful in the practice of the invention.

FIG.4 is a general side view of another type of high temperature gasification agent generator using a very lean catalytic combustor regenerator which is
representative of the heat exchanger useful in the practice of the invention. It
generates high temperature air/steam for gasification medium.

FIG.5 is a general block flow diagram of the gasifying facility as shown in
FIG.1.

FIG.6 is a generalized block flow diagram illustrating a modification of the
gasifying facility as shown in FIG.1. It illustrates a gasification process combining
a gasifier and hot gas treatment facility under the presence of Ca-based CO$_2$
sorbents.

FIG 7 is a generalized block diagram of an exemplary gasification process
according to an embodiment of the invention in FIG.6.

FIG 8 is a generalized block diagram of an exemplary gasification process
according to an embodiment of the invention in FIG.5.

FIG 9 is a generalized block diagram of an exemplary high temperature
air/steam gasification facility gasification process according to the invention.

FIG 10 shows gasifier structure and temperature measurement points.

FIG 11 shows LHV of product gas as a function of operational parameters
(large scale continuous experiment)...

FIG 12 shows concentrations of tar species in product gas.

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**DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS THEREOF**

The invention herein is a method and apparatus for gasifying a solid
material. The method comprises: a) providing at least one high heat source to
supply energy for gasification in a gasifier containing the solid material, resulting
in gases including CO$_2$ and hydrogen gas, and particulates, the heat source provided
by a method selected from the group consisting of: i) feeding a high temperature
gasifying agent in excess to supply required extra heat into the gasifier; and ii)
utilizing a Ca-based CO$_2$ absorbent to supply exothermic reaction heat; b)
separating hydrogen gas from the particulates in a separator; and c) recovering the
Ca-based CO$_2$ absorbent by a heating step, wherein the gasifier is at atmospheric

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pressure, and wherein complete combustion is increased in the gasifier. The solid material is preferably selected from the group consisting of coal, petroleum coke, biomass, and solid waste.

The preferred Ca-based CO$_2$ absorbent is CaO, which is added to the gasifier together with the solid material and the high temperature gasifying agent, and the gasifier is at 600-900°C. The preferred high temperature gasifying agent is selected from the group consisting of steam, air and oxygen and combinations thereof. When the high temperature gasifying agent is pure steam, a single gasification reactor is preferably used to produce a high level of hydrogen gas.

When the high temperature gasifying agent is a mixture of components selected from the group consisting of steam, air and oxygen, the gasification preferably utilizes two reactors, a first reactor to thermally decompose solid fuel to produce gases, solid materials and excess steam, and a second reactor to produce a hydrogen-rich gas.

The gasification apparatus of the invention preferably comprises: a) a high temperature gasifying agent generator, b) a gasifier, c) a solid gas separator, and d) a combustor for regeneration of sorbent. The high temperature gasifying agent generator may comprise at least one of: a heat exchanger, a combustor and a mixer, to generate a high temperature gas with a temperature in the range of 800 to 1600°C.

As discussed in more detail below, the disclosed invention herein is thus a biomass gasification system where high temperature steam/air is used as gasification agent in a first reactor, up-draft reactor, for production of a syngas. Optionally, the steam can contain a little amount of air/oxygen. Using no air, an almost N$_2$ free hydrogen gas is obtained. A high temperature is used as this favors the formation of hydrogen. The heat for the endothermic processes is supposed to be provided by the hot steam and optionally additional agents. For heating the hot steam and/or other agents either a honey-comb heat regenerator or a ball heat exchanger is used.
The produced syngas may enter a second reactor, a fluidised bed, together with CaO from a calciner. Alternatively CaO is added to the gasification process. CaCO$_3$ is produced as particles among the syngas in the fluidised bed/gasifier. Steam can optionally be added to the fluidised bed to convert remaining CO into CO$_2$ and hydrogen. The syngas containing CaCO$_3$ particles is let into a cyclone where CaCO$_3$ drops out into a calciner, where CaO is regenerated and CO$_2$ collected. The temperature in the gasifier is above 1000°C (1273K) and in the fluidised bed around 650°C (923K).

The total system of the present invention comprises two major parts: firstly a high temperature steam/air/oxygen generator, and secondly a gasification apparatus. (See Fig. 1)

The high temperature steam/air/oxygen generator can be comprised of:

- A heat exchanger, or
- A combustor or
- A mixer

either alone or any combination of them. The aim is generating a high temperature gas with a temperature in the range of 800 to 1600°C.

The gasification apparatus can be comprised of:

- A gasifier with a Ca-Based CO$_2$ sorbents (Fig. 2), or
- A gasifier and a hot syngas treatment facility gasifier with a Ca-Based CO$_2$ sorbent (Fig. 3),

The advantages of the disclosed invention are:

- Much less feedstock needs to be burnt to supply the necessary energy compared to prior techniques. This is because sensible energy is provided to the process with the highly preheated agent, and heat released by the chemical reaction between calcined lime and carbon dioxide. The process can thus be run with a lower oxidant to fuel ratio which leads to lower concentrations of diluents such as CO$_2$ and N$_2$ in the product gas and thus a higher heating value.
• High heating promotes the steam reforming reactions $\text{C}_x\text{H}_y + x\text{H}_2\text{O} \rightarrow x\text{CO} + (x+y/2)\text{H}_2$ and the formation of light gases in the thermal decomposition of the feedstock.
  • Enhanced heat transfer causes shorter residence time of the biomass in the gasification process.
  • A system less sensitive to the variability in particle size, heating value, and moisture content typically found in biomass feedstock.
  • The gasifier system can be built extremely compact at even atmospheric pressure, lowering component costs.

• Medium and High LCV value of syngas.
• High content of hydrogen in the syngas.
• Higher gas yields.
• Lower tar contents.
• Lower soot and char residues.

It is to be understood that the invention is not limited in its application to the details of construction and to the arrangements of the components set forth in the following description or illustrated in the drawings. The scope of the invention comprises embodiments and other ways of practicing and carrying out the invention. Also, it is to be understood that the phraseology and terminology employed herein are for the purpose of the description and should not be regarded as limiting.

Referring now to the figures, FIG.1 is a generalized flow diagram illustrating a preferred arrangement of the first type of embodiment of a solid fuel gasifying apparatus according to the invention. A gasification facility includes a high temperature gasifying agent generator, a gasifier, optionally a shift reactor (reformer, not shown), a gas-solid separator (cyclone), and a regenerative combustor (calciner).

The high temperature gasifying agent generator heats high temperature gases, such as air, steam, oxygen, exhaust gas, or a combination of them, to a temperature in the range of $800^\circ\text{C}-1600^\circ\text{C}$. This generator is comprised by three
components: a heat exchanger, a combustor, and a mixer, which can be used either alone or in any combination thereof. A high temperature gas (steam/air/oxygen) is obtained from a low temperature gas which passes through this heat exchanger.

When this heat exchanger is a normal metal heat exchanger, the temperature after the heat exchanger is around 300-500°C. When a regenerative heat exchanger is used, this temperature can be in the range of 800-1200°C. In order to achieve a higher temperature, an additional burner/combustor is used. The exhaust gas temperature can be 2600°C when an oxyfuel burner is used. Normally the temperature of this exhaust gas is around 1500-2000°C. In order to achieve a certain temperature for the gasifier, both hot streams will be mixed in a mixer. The temperature after the mixer is in the range of 800-1600°C.

When pure steam is needed for the gasification process only the heat exchanger is used. The temperature will be in the range of 600-1200°C.

The hot stream coming from the mixer is then charged into the gasification apparatus. Here the gasification apparatus is defined as a gasifier and optionally a shift reactor (reformer). There will be two technical solutions depending on the gasification agents in this invention: One is where pure steam is used as gasification agent, and another is where a steam/air/oxygen mixture is used.

In the case when CaO is mixed with feedstocks (FIG.5) only one gasification reactor is required. Here, the gasifier and the shift reactor (reformer) are integrated into one reactor. The main amount of pure steam is used for the gasification of solid fuel maybe as simply as:

\[ C_nH_m + H_2O \rightarrow nCO + (n+m/2)H_2 \]  (1)

The water-shift reaction is often used in order to get a high \( H_2 \) contents in the produced syngas:

\[ CO + H_2O \rightarrow CO_2 + H_2 -41.5 \text{ kJ/mol} \]  (2)

According to the disclosed invention the energy required for gasification process comes from:

1) Sensible heat carried by high temperature steam (over 800°C), and

2) Exothermic reaction of \( CO_2 \) absorption with a CaO sorbent:
CaO+CO₂ → CaCO₃ -178 kJ/mol (3).

The temperature of this reactor is maintained at 873-923 K (600-650°C) to enable carbonization of CaO, i.e. to absorb CO₂. Simultaneously, the CO₂ partial pressure is reduced by CaO (eq3). This leads to an improvement of the hydrogen production in the produced gas.

Since the equilibrium CO₂ partial pressure at 873 K is 0.004 atm over 90% of the CO₂ can be absorbed in the reactor, whose CO₂ partial pressure is approximately 20-40% if high temperature pure steam is used. It should be noticed that Ca(OH)₂ formation does not occur in the absorber since the equilibrium pressure of H₂O of Ca(OH)₂ (eq 4) formation is higher than 1 atm at 873 K (600°C).

CaO+H₂O→Ca(OH)₂  (4)

The produced CaCO₃ is transported to the regenerator. In the regenerator, the temperature is maintained at 1223K (950°C). At this temperature, the equilibrium CO₂ partial pressure is 1.9 atm and the reverse reaction of equation (3) takes place even when the concentration of CO is over 90% at atmospheric pressure, as follows:

CaCO₃ → CaO +CO₂  (5)

Since the calcination (Eq5) is an endothermic reaction, the heat for the calcination of CaCO₃ is supplied by the combustion of a part of the syngas, and of the char from the gasifier.

In the case where CaO is added into the gas clean system (FIG.6) the gasification apparatus comprises two reactors: one gasifier and one shift reactor (reformer).

In the gasifier, the solid fuel is thermally decomposed to produce the syngas using the sensible heat of high temperature gasifying agent (steam/air/oxygen) (600-1200°C), and the heat generated by an exothermic oxidation reaction between the high temperature air and solid fuel. The produced gas comprises gases, such as CO, H₂, light and heavy hydrocarbons, and solid materials, such as tar. In particular, a larger excess of high temperature steam is generated.
The gasified gas and tar containing the surplus of steam from the gasifier then enter a reformer with CaO injection. This reformer is operated at 650°C. CO₂ is captured by CaO, and this promotes the water-shift reaction, and steam reforming reaction, thus a hydrogen-rich gas is obtained. This reformed gas and CaCO₃ pass a gas-solid separator. The spent Ca-based sorbents can be regenerated by calcination at high temperature (1173K (900°C)). The calcined sorbents are supposed to be reused for CO₂ sorption in the reformer. The heat for the calcination of CaCO₃ is supplied by combustion of a part of syngas.

In this system, the water-gas shift reaction can take place in a mild temperature (approximately 973K (700°C)) since the CO₂ is absorbed by the carbonation reaction, thus a low CO₂ partial pressure can promote the water shift reaction. Simultaneously, this results in the substantial increase in H₂ yield in the product gas.

FIG.2 is a general side view of a heat exchanger to heat a low temperature gas (steam/air/oxygen) up to 1000°C using a ball type regenerator which is representative of the heat exchanger useful in the practice of the invention. The generator comprises two chambers. In each chamber, there is a normally a burner in the upper part of the chamber, while in the ball type regenerator it is located at the bottom of the combustion chamber. The system runs in two models. For example, when the burner A (left) starts to work, the hot exhaust gas generated by combustion at 1200-1400°C passes through the void spaces between the regenerative balls. This hot exhaust gas is cooled down to a temperature as low as 200°C. The heat carried by the hot exhaust is stored in the regenerative balls. At a certain time, say 50-100s, the burner A (left) is shut down, and a low temperature saturated steam/air/oxygen) is fed from the bottom of the regenerative balls. This low temperature gas is heated up to 900-1300°C when it passes through the regenerative balls. The preheated gas temperature can be 100-300°C lower than that of the regenerative balls, say 800-1000°C. This hot stream leaves the heat exchanger from the top of the chamber. In order to obtain a continuous high
temperature stream, two chambers are integrated. When the left chamber serves as a combustion chamber the right chamber works as a heat exchanging chamber.

Heat storage and heat release in the regenerators are repeated periodically when combustion gas and low temperature gas are alternately provided by on-off action of a switching valve located on the low temperature side. The preheated gas continuously discharges from an exit nozzle at the right hand side section, and combustion gas exhaust from the left hand side section as shown in the figure.

FIG.3 is a general side view of another type of heat exchangers to heat a low temperature gas (steam/air/oxygen) up to 1300°C using a rotary honeycomb type regenerators which are representative of the heat exchangers useful in the practice of the invention. The ultra-high temperature air/steam generator comprises two chambers and a rotary regenerative honeycomb heat exchanger. In this generator, only one is combustion chamber, and another is a heat exchanging chamber. In this drawing, the left chamber is a combustion chamber. In the top of this chamber, a normal gas-burner is used to generate high temperature flue gas, which can be as high as 1500K (1223°C) depending on the fuel and burner. This hot flue gas pass though the rotary regenerator, the heat is stored in the regenerator and the temperature of flue gas is cooled to around 120°C when it leaves the system. The temperature of regenerator can be heated up to 1100-1300°C. Hot part regenerator is rotated to the other chamber (see FIG. 3). Low temperature air and/or low temperature saturated steam is injected into this hot regenerator, and is heated to a temperature only 50-80 °C lower than that of the regenerator. i.e., the temperature of air and/or steam can be preheated up to 1250°C.

Heat storage and heat release in the regenerators are repeated periodically when combustion gas and low temperature steam/air are alternately provided by a rotary action, a continuous ultra-high temperature steam/air can be obtained.

FIG.4 is a general side view of another type of high temperature gasification agent generator using a very lean catalytic combustor regenerator which is representative of the heat exchanger useful in the practice of the invention.
A typical catalytic combustor working in very lean condition can also supply high temperature gas for the gasification process.

Here, when normal gas fuel, for example LPG is used, an excess air ratio can be 3-6 when air is used as oxidizer. Here, we can generate a temperature of 900-1200°C with the concentration of the mixture as follows: 17.3% of O2, 77.9% of N2, 2.8% of H2O (vapor) and 2.1% of CO2. (the excess air ratio is 5). This can be also used for the gasification process.

In order to get a high content of steam in this exhaust gas, a hydrogen rich fuel /or pure hydrogen fuel can be used.

FIG.5 is a general block flow diagram of the gasifying facility as shown in FIG.1. The system includes a gasifier, a gas-solid separator, and a combustor for regeneration of Ca-based sorbent. The feedstock (solid fuel such as coal, biomass and/or waste), and Ca-based sorbent (CaO), and ultra high temperature steam/air are fed into a gasifier. The produced stream, gas (syngas) and solid particles (tar, and CaCO3), enter a separator for separation of gases and solids. The solid materials, which comprise mainly CaCO3, enter a reactor, and the thus spent Ca-based sorbents can be regenerated by calcination at high temperature such as 1273K.

FIG.6 is a generalized block flow diagram illustrating a modification of the gasifying facility as shown in FIG.1. A high temperature gasification agent is fed into a gasifier, the thermal decomposition gas from the solid fuel flows into a hot gas treatment facility, together with/without high temperature steam. There, the gasified gas and tar containing much steam provided by the gasifier then enter a fluidized bed reformer with CaO injection. This reformer is operated at 650°C. CO2 is captured by CaO, and this promotes the water-shift reaction, and steam reforming reaction, thus a hydrogen-rich gas is obtained. This reformed gas and CaCO3 pass a cyclone gas-solid separator. The spent Ca-based sorbents can be regenerated by calcination at high temperature (1173K (900°C)). The calcined sorbents are supposed to be reused for CO2 sorption in the reformer. The heat for the calcination of CaCO3 is supplied by combustion a part of syngas.
FIG 7 is a generalized block diagram of an exemplary gasification process in accordance with an embodiment of the invention in FIG.6. A high temperature (900-1300°C) gasification agent is fed into a gasifier, and the thermal decomposition gas from the solid fuel flows into a hot gas treatment facility together with/without high temperature steam, the gasified gas and tar containing much steam provided by the gasifier enter a fluidized bed reformer with CaO injection. This reformer is operated at 650°C. CO₂ is captured by CaO, and this promotes the water-shift reaction, and steam reforming reaction, thus a hydrogen-rich gas is obtained. This reformed gas and CaCO₃ pass a cyclone gas-solid separator. The spent Ca-based sorbents can be regenerated by calcination at high temperature (1173K). The calcined sorbents are supposed to be reused for CO₂ sorption in the reformer. The heat for the calcination of CaCO₃ is supplied by combustion a part of syngas.

FIG 8 is a generalized block diagram of an exemplary gasification process in accordance with an embodiment of the invention in FIG.5. The feedstock (solid fuel such as coal, biomass and/or waste) first enters a mixer and is mixed with the sorbent (CaO), then, it is fed into a fixed bed reactor. An ultra-high temperature steam/air (over 900°C) is generated by a heat exchanger, e.g. a regenerative heat exchanger, and flows into the bottom of the fixed bed reactor. The produced gas enters a cyclone to separate gas stream and solid materials. The solid materials, which mainly comprise CaCO₃, enter a reactor, and this spent Ca-based sorbents can be regenerated by calcination at high temperature according to:

\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2
\]

Here the calcined sorbents are supposed to be reused for CO₂ sorption in the reformer. The heat for the calcination of CaCO₃ is supplied by combustion a part of syngas.

FIG 9 is a generalized block diagram of an exemplary gasification process in accordance with the invention, a continuous counter-current updraft fixed-bed gasifier.
The fixed-bed gasifier used in this example is shown in FIG. 10. A highly preheated air generator is used to preheat air or steam up to 1200°C. This generator can be bought, for example, from Nippon Furnace CO. Ltd., Japan. An additional burner for oxidizer temperature can further rise the temperature of steam/air up to 1600°C. A fuel feeding system consists of feedstock hopper, feeding screw, and two electric motors.

An electrical steam boiler to produce slightly preheated steam (180°C, 2.5 bar), equipped with a water preparation unit.

An air blower is used to supply air into preheater and subsequently to the gasifier.

A fluidized bed reformer (1) is connected after the gasifier. In this reactor, the syngas generated from the gasification system enters the bottom of the reactor. A gas distributor (3) is used. The limestone is injected above the distributor. The high-temperature steam from high-temperature steam generator can be injected depending on the quantity and the temperature of the steam in the syngas.

A cyclone (11) is used to separate the produced gas from solid/particle including the CaCO₃. The cyclone is temperature isolated to prevent condensed tars and water. Separated particles are stored in a container (13).

A kiln (15) is used for calcination of CaCO₃. In order to regenerate the limestone, the temperature in the kiln should be higher than 900°C. Here, a normal gas burner(16), for example, a part of produce syngas, is used to supply the heat to the process.

After regeneration of the sorbent, it is first stored in a chamber (17), then transported by screw feeders (4) and (5) to the reformer. The fresh limestone can be added into this chamber (17) after several cycles of using. The quantity of Sorbents injecting to the reformer is adjusted according to the measurements of CO₂ concentration/partial pressure and the temperature before (9) and after (10) reactor(1).

Temperature in the reformer chamber is one of key parameters to control the steam reforming process based on the presence of CO₂ sorbents. The favorable
operation temperature in the reformer is in the range of 600-900°C. The Syngas
temperature from the outlet of gasifier can go up to 1200°C since a high-
temperature air/steam agent is used. In this example, the temperature in the
reformer (1) is monitored by thermocouple (8) and it can be adjusted by the heat
exchanger (2).

For process control and safety reason pressure meters are installed (7).

The normal valves (6, 14 and 18) are installed in the connecting places of
the individual elements of the system. A siphon-trap (12) is installed between the
cyclone and the CaCO3 storage chamber (13).

FIG 10 is an example of the updraft fixed bed gasifier used in fig. 9 with
the temperature measurement points which are used for the gasifier control. It is a
vertical cylindrical reactor which consists of six sections:
- SB - slag box serving as slag collector
- WB - wind box
- PB - grate and pebble bed part
- BP - bed part, feedstock (fixed bed) section
- GPP - gas phase part, fuel gas outlet section
- top - section of feedstock feeder.

The high-temperature air/steam is injected into the gasifier from the left –
bottom, and the feedstock(biomass) enters the gasifier from the top of the gasifier.
The produced gas leaves the gasifier from the right-top. The temperature of wind
box, gas phase part of the gasifier, and the produce gas are monitored by the
thermocouple.

As to a further discussion of the manner of usage and operation of the
present invention, this should be apparent from the above description.
Accordingly, no further discussion relating to the manner of usage and operation
will be provided.

With respect to the above description then, it is to be realized that the
optimum dimensional relationships for the parts of the invention, to include
variations in size, materials, shape, form, function and manner of operation,
assembly and use, are deemed readily apparent and obvious to one skilled in the art.

Therefore, the foregoing is considered as illustrative only of the principles of the invention. Further, since numerous modifications and changes will readily occur to those skilled in the art, it is not desired to limit the invention to the exact construction and operation shown and described, and accordingly, all suitable modifications and equivalents may be resorted to, falling within the scope of the invention.

Example 1: High-temperature air/steam gasification with hot gas treatment under the presence of Ca-Based CO₂ sorbents

One example of embodiment of the invention is the high-temperature air/steam gasification with hot gas treatment under the presence of Ca-Based CO₂ sorbents.

A generalized block diagram of the gasification process is shown in FIG 7. The apparatus used includes:

- An updraft fixed bed gasifier. Here it is a cylinder manufactured by ceramic high-temperature materials with the work temperature up to 1500°C, for example, produced by Calders Refractory Solutions Company.

In this gasifier, high-temperature air/steam is supplied from the gasifier bottom, and the feedstock (biomass) is fed from the top of the gasifier.

- A fluidized bed reformer
- A cyclone made by normal steel, and
- A Calciner equipped by a normal burner.

In the method of the invention, the following process occurs: a high temperature gasification agent is fed into a gasifier, and the thermal decomposition gas from the solid fuel flows into a hot gas treatment facility, together with/without high-temperature steam. There the gasified gas and tar containing much steam supplied by the gasifier then enter a fluidized bed reformer with CaO injection.
This reformer is operated at 700 °C at atmospheric pressure. CO₂ is captured by CaO, and this promotes the water-shift reaction, and steam reforming reaction, thus a hydrogen-rich gas is obtained. This reformed gas and CaCO₃ pass a cyclone gas/solid separator. The spent Ca-based sorbents is regenerated by calcination at high temperature (1273K). The calcined sorbents are reused for CO₂ sorption in the reformer. The heat for the calcination of CaCO₃ is supplied, for example, by combustion a part of syngas.

More specifically, FIG. 9 is an exemplary high temperature air/steam gasification process system in accordance with an embodiment of the invention in FIG.7. In this equipment, air is supplied to the system by an air blower. Slightly preheated steam (180°C, 2.5 bar) produced by an electrical steam boiler is introduced to the air-line. The relative flow of the air and steam is regulated manually and monitored by a set of flow meters.

The temperature of the feed gas (air/steam mixture) is raised to over 1200°C by a regenerative preheater working in cycles in which the air/steam mixture passes through a hot honeycomb in one chamber while hot combustion gases are heated up in another chamber with a subsequent inversion of the flow. To obtain temperatures of the air/steam mixture up to 1400-1600°C, additional fuel (propane) is burned at the preheater outlet before the inlet to the reactor body.

The gasifier body in this example is a vertical cylinder with an inner diameter of 0.4 m and consists of five sections from bottom to top organized as shown in FIG. 10.

The materials used in this example are;

- Wood pellet is used as feedstock. The sizes of wood pellets are in the range of 6-12 mm.
- The temperature of steam and air is 1273K, and the ratio of steam to carbon is 1-2.
- The size of limestone using in the gas conditioning, CaO is in the range 300-400 μm. CaO absorbs 90% of CO₂ in the syngas at 700 °C and atmospheric pressure.
After the high-temperature air/steam gasifier (FIG. 9) the following data is obtained: The syngas gas with LHV of 7-9 MJ/Nm³ is produced via the disclosed invention using highly preheated air as feed gas from biomass (example in Fig. 11).

The concentration of H₂ in the product gas increases in response to increasing feed gas temperatures, in particular if steam is added to the feed gas. In fact, hydrogen concentrations, as high as 25-30%, are obtained from air/steam-HiTAG of wood pellets in the laboratory test.

Solid phase adsorption (SPA) is used to characterize the tar in the product gas from HiTAG gasification and preliminary results indicate decreasing tar amounts in response to increasing feed gas temperatures (Fig. 12). Small scale experiments also show that (in the presence of O₂ in low concentrations) the product gas yield gains with respect to both solid and liquid yield when the temperature of the feed gas is increased to HiTAG levels.

After coupling of HiTAG gasifier with hot gas treatment, 90% of CO₂ is removed at atmospheric pressure, and tar is further eliminated. The hydrogen concentration is in the range of 40-80%, and the HHV is in the range of 12-16 MJ/Nm³.

**Example 2: Biomass gasification using High-temperature air/steam and Ca-Based CO₂ sorbents**

One example of an embodiment of the invention is biomass gasification using high-temperature air/steam and Ca-Based CO₂ sorbents. A generalized block diagram of the gasification process is shown in FIG. 8. The apparatuses used are:

- An updraft fixed bed gasifier. Here it is a cylinder manufactured by a ceramic high-temperature material with the work temperature up to 1500°C, for example, produced by Calderys Refractory Solutions Company. In this gasifier, high-temperature air/steam is supplied from the gasifier bottom, and the feedstock (biomass) is fed from the top of the gasifier.
A steam heater. It is made by a regenerative honeycomb heat exchanged as shown in FIG. 9. After passing a saturated steam through the heat exchanger, the temperature of steam achieves 1200 °C generated by

- A mixer for the mixing of feedstock and limestone
- A cyclone made by normal steel, and
- A Calciner equipped by a normal burner.

In the method of the invention, the following process is occurring: The feedstock (solid fuel such as coal, biomass and waste) first enters a mixer and is mixed with the sorbents (CaO). Then it is fed into a fixed bed reactor. An ultrahigh temperature steam (over 1200°C) is generated by a heat exchanger, such as a regenerative heat exchanger, and flows into the bottom of the fixed bed reactor. The produced gas enters a cyclone to separate gas streams and solid materials. The solid materials, mainly CaCO₃, enter a reactor (calciner), and this spent Ca-based sorbents is regenerated by calcination at high temperature as:

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]

The calcined sorbents are reused for CO₂ sorption in the reformer. The heat for the calcination of CaCO₃ is supplied by combustion a part of syngas.

The gasifier body is a vertical cylinder with an inner diameter of 0.4m and a height of 0.75m.

The materials used in this example are;

- Wood pellet, which is a blend with limestone. The sizes of wood pellets are in the range of 6-12 mm.
- Pure steam with the temperature of 1173 K is used.
- The size of limestone, CaO, for the gas conditioning is in the range 300-400 μm. CaO absorbs 90% of CO₂ in the syngas in the range of 1173°C at atmospheric pressure.

The mass balances in the thermal gasification system in FIG. 8 are calculated using a computer program in order to estimate the steady state equilibrium. Wood pellets are used, and the cellulose is assumed to have a general chemical formula CH₁₂O₁₀₆₃₈.
The estimated results show that 90% of CO₂ is removed at atmospheric pressure, and tar is further very small, and there is no need for further treatment. The hydrogen concentration is in the range of 60-90%, and the HHV is in the range of 16-20 MJ/Nm³.
Claims

1. A method for gasifying a solid material, comprising:
   a) providing at least one high heat source to supply energy for gasification in a gasifier containing the solid material, resulting in gases including CO₂ and hydrogen gas, and particulates, the heat source provided by a method selected from the group consisting of:
      i) feeding a high temperature gasifying agent to supply heat into the gasifier; and/or
      ii) utilizing a Ca-based CO₂ absorbent to supply exothermic reaction heat;
   b) separating syngas from the particulates in a separator; and
   c) recovering the Ca-based CO₂ absorbent by a heating step, wherein the gasifier is at atmospheric pressure, and wherein complete gasification is increased in the gasifier.

2. The method of claim 1, wherein the solid material is selected from the group consisting of coal, petroleum coke, biomass, and solid waste.

3. The method of claim 1, wherein the Ca-based CO₂ absorbent is CaO.

4. The method of claim 3, wherein the CaO is added to the gasifier together with the solid material and the high temperature gasifying agent, and the gasifier is at 600-900°C.

5. The method of claim 3, wherein the CaO is added to a refining process of the produced gas for capturing the formed carbon dioxide in a second reactor, and the temperature of the second reactor is at 600-900°C.
6. The method of claim 1, wherein the high temperature gasifying agent is selected from the group consisting of steam, air and oxygen and combinations thereof.

7. The method of claim 6, wherein the high temperature gasifying agent is pure steam, and a single gasification reactor is used to produce a high level of hydrogen gas.

8. The method of claim 6, wherein the high temperature gasifying agent is a mixture of components selected from the group consisting of steam, air and oxygen, and the gasification utilizes two reactors, a first reactor to thermally decompose solid fuel to produce gases, solid materials and excess steam, and a second reactor to produce a hydrogen-rich gas.

9. A gasification apparatus comprising: a) a high temperature gasifying agent generator, b) a gasifier, c) a solid gas separator, and d) a combustor for regeneration of sorbent.

10. The gasification apparatus of claim 9, wherein the high temperature gasifying agent generator comprises at least one of: a heat exchanger, a combustor and a mixer, to generate a high temperature gas with a temperature in the range of 800 to 1600°C.

11. The gasification apparatus of claim 9, wherein the gasifying agent is selected from the group consisting of steam, air, oxygen, exhaust gas, and the combination thereof.

12. The gasification apparatus of claim 9, wherein the gasification apparatus is a gasifier with a Ca-based CO₂ sorbent.
13. The gasification apparatus of claim 9, wherein the gasification apparatus is a gasifier and a hot syngas treatment facility gasifier with a Ca-based CO$_2$ sorbent.

14. The gasification apparatus of claim 9, wherein the high temperature gasifying agent generator comprises an exchanger selected from the group consisting of a ball type regenerator, a rotary honeycomb type generator, and a catalytic combustor regenerator.

15. The gasification apparatus of claim 9, wherein the apparatus gasifier is a continuous counter-current updraft fixed bed gasifier, the high temperature gasifying agent is preheated by a preheated air generator, and the apparatus further comprises a cyclone is used to separate produced gas from solid material, and a kiln for calcination of CaCO$_3$. 
Figure 3

Fuel & Air

Hight-temperature Air/ Steam

Flue Gas Air/ Saturated Steam
Figure 4

Gas Fuel

air/oxygen enriched gas

Pre-Mix

steam

Catalytic Combustor

High-temperature oxidizer (air/oxygen, steam)
Figure 5
Figure 6
Figure 7
Figure 8
Figure 10
Figure 11
Figure 12